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X-Ray Study of Calcium Ammonium Nitrate

By

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An attempt has been made to elucidate the nature of the fertilizer, calcium ammonium nitrate. The results given in this paper include data on its crystal-phase composition, the nature of the impurities and the estimation of calcium nitrate tetrahydrate present in it.

Introduction

Ammonium nitrate is an important and widely used fertilizer because of its higher nitrogen content. But its use as such is limited by its potentially explosive character and hygroscopicity[1]. The pure ammonium nitrate contains about 35 per cent nitrogen, and its explosive character can be reduced by diluting it with an inert material, like limestone, dolomite, dolomitic limestone, gypsum, etc.

Chemicals manufacturers in many countries[2] are already producing calcium ammonium nitrate, usually known as CAN, which is a mechanical mixture of ammonium nitrate and limestone in the near about 60: 40 ratio, with overall 20.5 per cent nitrogen. Two fertilizer plants, viz. at Rourkela (Orissa) and Nangal (Punjab), in India are also producing calcium ammonium nitrate. The caking characteristics of calcium ammonium nitrate have been studied in this laboratory and elsewhere, and it has been found that CAN is slightly more hygroscopic than ammonium nitrate. It has also been reported that the presence of calcium nitrate, preferably about 1 per cent, is advantageous in the product which minimizes its caking tendency.[3, 4]

The present investigation was undertaken with a view to obtain more information on the physical nature of the fertilizer, calcium ammonium nitrate, with particular reference to its crystal-phase composition, the nature of impurities present in it and the estimation of calcium nitrate associated with it. All these data are necessary to assess this fertilizer.

Experimental

Materials Used: Samples of calcium ammonium nitrate were obtained from the Rourkela and Nangal units of FCI Ltd.

Chemical Composition: The composition of calcium ammonium nitrate is approximately as follows: limestone 40 (80 per cent passing through 100 mesh B.S.); NH_4 NO_3 60; and soapstone used as coating material 0.3-0.4 per cent (80 per cent passing through 300 mesh).

X-ray Analyses: The x-ray diffraction pattern of the samples were recorded in a Philips camera of diameter 11.46 cm. with Philips x-ray unit, PW1010 (Fig. 1). CuK_α radiation with nickel filter was used, the x-ray tube operated at 40 kV with 20 ma The time of exposure to each sample was 3 hr. The intensities of lines on the x-ray powdered photographs for the phase identification were estimated visually, and the phase identification was done by the usual method of Hanawalt et al[5]. The Philips x-ray diffractometer PW 1050/51 was used for quantitative analysis.

Results & Discussions

Identification of Phases: The x-ray diffraction data are given in Tables 1 & 2. The x-ray analyses of both coated and uncoated sample show the presence of ammonium nitrate IV type, calcite, calcium nitrate tetrahydrate and dolomite. In order to detect the impurities, the samples were treated with acetic acid, and the x-ray photographs of the residues were then taken. In the coated sample of CAN, impurities like quartz and talc were detected, while in the uncoated only quartz could be detected.

The probable role of calcium nitrate in the body structure of calcium ammonium nitrate is worthy of discussion. In this study the amount of $Ca\ (NO_3)_2 \cdot 4H_2O$ in CAN has been found low as indicated by the relative intensity of their diffraction pattern.

The existence of different phases of ammonium nitrate and their transformations from one to other is well established.[6-8] The transition of the phases which are of interest in fertilizer manufacture is from III$\longleftrightarrow$IV.

TABLE 1—PHASES IDENTIFIED IN CALCIUM AMMONIUM NITRATE

Sl. No.	Name of the Substance	Crystalline Phase
1	Calcium ammonium nitrate (coated) Rourkela variety	NH_4 NO_3 IV type, calcite, calcium nitrate tetrahydrate and Dolomite
2	Do (uncoated)	NH_4 NO_3 IV type, calcite, calcium nitrate tetrahydrate and Dolomite
3	Do (impurities) Rourkela variety (uncoated)	Quartz
4	Do (coated)	Quartz and Talc
5	Calcium ammonium nitrate (coated) Nangal variety	NH_4 NO_3 IV type, calcite, calcium nitrate tetrahydrate and dolomite
6	Do (uncoated)	NH_4 NO_3 IV type, calcite, calcium nitrate tetrahydrate and Dolomite
7	Do (impurities) Nangal variety (uncoated).	Quartz
8	Do (coated).	Quartz and Talc

Phase IV is stable from $-18°$ to $32°C$ ($-0.4°$ to $89.6°F$) and phase III is stable from $32°$ to $84°C$ ($89.6°$ to $183.2°F$). Both the modifications are of orthorhombic system, but the lattice parameters decreases when transformed from III to IV. It is well-known that one of the causes of the hard setting of ammonium nitrate is due to its phase transition occuring above 32°C. It is to be noted, however, that the diffraction pattern of each sample studied exhibits the presence of lines due to NH_4 NO_3 IV phase, and no lines due to phases like the solid solution or a double salt of ammonium nitrate-calcium nitrate system are found[9,10]. Again, the presence of free NH_4 NO_3 IV in the diffraction pattern reveals that Ca $(NO_3)_2$ and other impurities present in the system do not affect the transition temperature of NH_4NO_3 IV$\leftarrow\rightarrow$III.

Estimation of Calcium Nitrate Tetrahydrate: The quantitative analysis by x-ray diffraction is based on the fact that the intensity of a diffraction line characteristic of the substance under consideration depends on the concentration of the substance in the mixture. The concentration of the unknown is obtained by a calibration curve which relates to the known concentration of the substance. The concentration of the substance

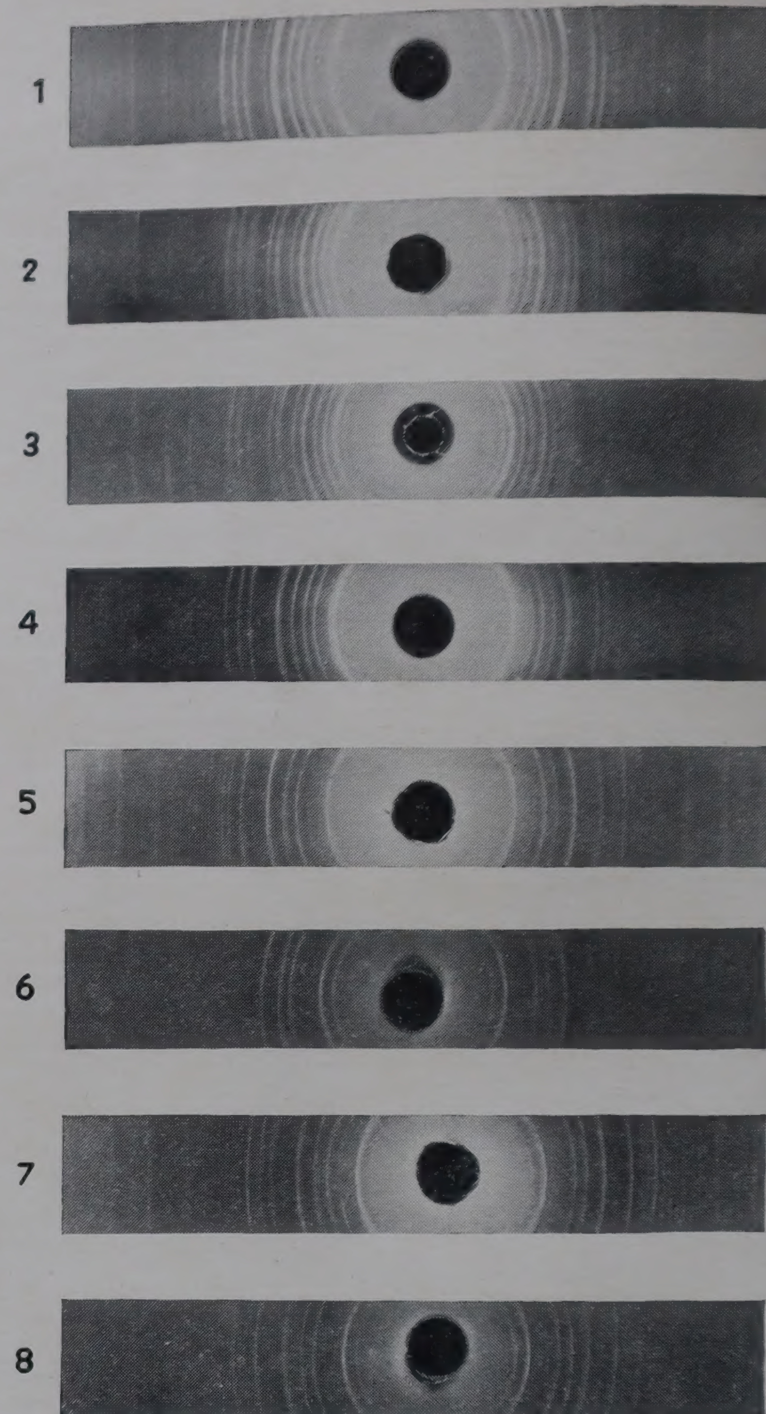

Fig. 1. X-ray Photographs of Calcium Ammonium Nitrate.

Radius of camera—5.75 cms. Radiation of CuKα —1.540 A

Time of exposure—6 hours.

1. CAN (Coated) Nangal variety.
2. CAN (Uncoated) Nangal variety.
3. CAN (Coated) Rourkela variety.
4. CAN (Uncoated) Rourkela variety.

Insoluble residue after treatment with acetic acid.

5. Can (Coated) Nangal variety.
6. CAN (Uncoated) Nangal variety.
7. CAN (Coated) Rourkela variety.
8. CAN (Uncoated) Rourkela variety.

TABLE 2—X-RAY DATA ON CALCIUM AMMONIUM NITRATE

Calcium Ammonium Nitrate (Rourkela Variety)				*Calcium Ammonium Nitrate (Nangal Variety)*				*Calcium Ammonium Nitrate Residue after Acetic Acid Treatment*			
Coated		*Uncoated*		*Coated*		*Uncoated*		*Coated*		*Uncoated*	
dÅ	1	dÅ	1	d	1Å	dÅ	1	dÅ	1	dÅ	1
3.95	w	3.95	w	5.60	m	5.60	m	3.71	vvw	4.28	vvw
3.41	m	3.40	m	4.04	ms	4.04	ms	3.34	vvw	3.77	vvw
3.09	s	3.09	s	3.10	s	3.10	s	3.02	vvw	3.41	w
2.88	vvw	2.88	vvw	2.89	vvw	2.89	vvw	2.87	s	3.23	vvw
2.79	m	2.79	m	2.80	ms	2.80	ms	2.69	vvw	3.13	vvw
2.53	w	2.53	w	2.54	w	2.53	w	2.55	vvw	3.01	ms
2.43	vw	2.43	vw	2.44	vw	2.44	vw	2.42	vvw	2.89	s
2.28	ms	2.28	ms	2.29	ms	2.29	ms	2.21	w	2.71	vvw
2.11	m	2.11	m	2.12	m	2.12	m	2.08	vvw	2.57	vvw
2.01	vvw	2.01	vvw	2.01	vvw	2.01	vvw	2.03	vw	2.47	vvw
1.94	m	1.94	m	1.94	m	1.94	m	1.86	vvw	2.42	vw
1.89	m	1.88	m	1.90	m	1.89	m	1.82	ms	2.31	vvw
1.81	vw	1.81	vw	1.82	vw	1.82	vw	1.80	ms	2.22	ms
1.64	vw	1.64	vw	1.64	vw	1.63	vw	1.58	vvw	2.16	vvw
1.60	vw	1.60	vw	1.60	vvw	1.60	vvw	1.56	vw	2.09	vvw
1.53	vw	1.54	vw	1.54	vw	1.54	vw	1.48	vw	2.04	w
1.48	vvw	1.48	vvw	1.49	vvw	1.49	vvw	1.46	vw	1.87	vvw
1.44	vw	1.45	vvw	1.46	vw	1.46	vw	1.44	vw	1.83	w
1.38	vvw	1.38	vvw	1.39	vvw	1.38	vvw	1.42	vvw	1.81	w
1.34	vvw	1.33	vvw	1.32	vvw	1.31	vvw	1.40	w	1.69	vvw
1.18	vw	1.19	vvw	1.19	vw	1.19	vvw	1.35	vw	1.59	vvw
1.16	m	1.16	m	1.17	m	1.16	m	1.31	vvw	1.56	w
1.05	m	1.05	m	1.06	m	1.05	m	1.28	vw	1.52	vvw
1.01	vvw	1.01	vvw	1.02	vvw	1.02	vvw	1.25	vw	1.48	vw
								1.21	vvw	1.40	vw
								1.18	vvw	1.39	vvw
								1.13	vvw	1.35	vw
								1.12	w	1.31	vvw
								1.11	vvw	1.28	vvw
								1.01	vw	1.24	vvw
										1.21	vvw
										1.19	vvw
										1.18	vvw
										1.13	vvw
										1.12	w
										1.01	vvw
										1.00	vvw

s=strong; ms=medium strong; m=medium; w=weak; vw=very weak; vvw=very very weak.

in an unknown sample can be obtained by measuring the intensity for a composite sample containing the unknown from the calibration curve.

Philips x-ray diffractometer PW 1050/51 with Geiger counter as detector and filtered CuKα radiation with nickel filter were used for the quantitative analysis. Line intensities were determined from the Geiger counts, setting the Geiger tube position manually at the desired angle. The integrated intensity measurement was found suitable for the measurement of the calcium nitrate tetrahydrate content. The operating conditions for the diffractometer were as follows: x-ray tube 40kV, 20 ma., detector Geiger Muller Counter tube, 1650 V; Multiplication 1; scale selector 64; time constant 2 secs; scatter slit 1°; receiving slit 0.2 mm; divergence slit 1°; scanning speed 1° per min; and paper speed 200 mm/hr.

Four synthetic samples of CAN each containing 1.5, 2.5, 3.7 and 5.5 per cent of calcium nitrate tetrahydrate respectively were prepared in weight per cent basis under identical conditions. The intensity of the 2.81Å ($2\theta=31.84°$) calcium nitrate tetrahydrate maximum was used as reference line for intensity measurement. But since this line is interfered by a weak line of ammonium nitrate in the angular position $31.16°=2\theta$ (d= 2.87 Å), it was necessary to subtract the ammonium nitrate reinforcement from the intensity at $31.84°=2\theta$. In order to estimate this reinforcement, it was considered preferable to base the calculations on the intensity measurements at 31.84° and 33.1° (a non-reinforced ammonium nitrate peak) so that any differences in measurement for a number of determinations caused by variation in crystal orientation is prevented. If, I_a and I_b be the intensities of the samples at $33.1°=2\theta$ and $31.84°=2\theta$, and I_c and I_d the intensity of pure ammonium nitrate at $33.1°=2\theta$ and $31.16°=2\theta$, then the correction for the ammonium nitrate reinforcement is $I_a \times I_d/I_c$. The corrected calcium nitrate tetrahydrate intensity will therefore be $I_b - I_a \times I_d/I_c$ (Table 3). From the relationship of the corrected calcium nitrate tetrahydrate intensities with the concentrations of the calcium nitrate tetrahydrate, it can be seen that although the intensities are corrected for background counts, the calibration curve does not pass through the origin (Fig. 2). This extra intensity is caused by the non-x-ray background. Counter tube, circuit noise, cosmic rays and radioactivity all contribute to the non-x-ray background. By referring to Fig. 2, the corrected intensities of the unknown samples of CAN Rourkela and Nangal varieties, were then used to determine the calcium nitrate tetrahydrate present in them (Table 4). From the observed intensity, the amount of calcium nitrate tetrahydrate found is approximately 1.18 per cent in Rourkela variety and 1.2 per cent in the Nangal variety (Table 5). An illustration of the diffractometer curve is shown in Fig. 3.

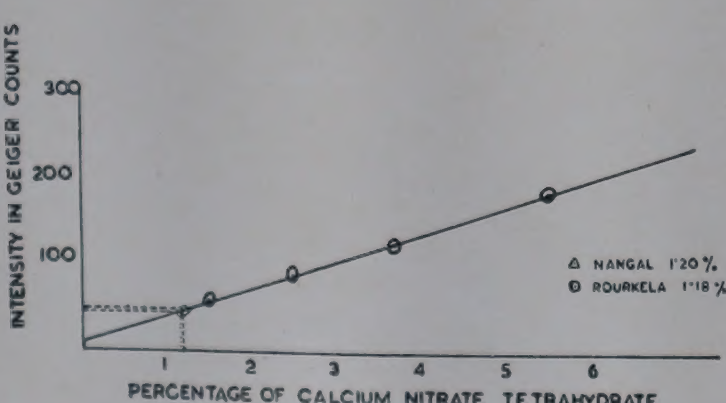

Fig. 2. Curve for Determination of Calcium Nitrate Tetrahydrate in CAN.

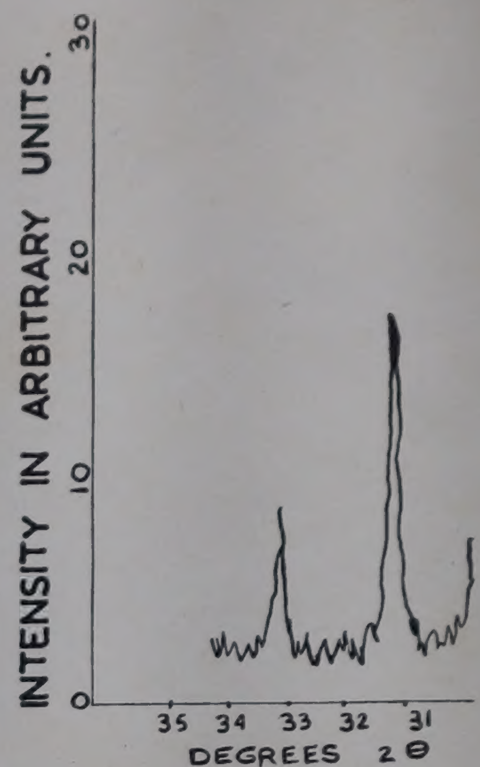

Fig. 3. Diffractometer Curve for Estimation of $CaNO_3.4H_2O$ in CAN.

TABLE 3—INTENSITY MEASUREMENTS OF SYNTHETIC SAMPLES OF CALCIUM AMMONIUM NITRATE CONTAINING CALCIUM NITRATE TETRAHYDRATE

(All values corrected for the background)

$Ca(NO_3)_2\ 4H_2O$ in CAN, %	$I_a \times I_d/I_c$	I_b	Corrected $Ca(NO_3)_2\ 4H_2O$ intensity $I_b-(I_a \times I_d/I_c)$
1.5	412	477	65
2.5	411	504	93
3.7	411	537	126
5.5	412	597	185

TABLE 4—INTENSITY MEASUREMENTS OF TWO SAMPLES OF CALCIUM AMMONIUM NITRATE

(All values corrected for background)

Sl. No.	Sample of CAN	$I_a \times I_d/I_c$	I_b	Corrected intensity of $Ca(NO_3)_2\ 4H_2O$ $I_b-(I_a \times I_d/I_c)$
1	Nangal	412	462	50
2	Rourkela	413	461	48

TABLE 5—CALCIUM NITRATE TETRAHYDRATE IN DIFFERENT SAMPLES OF CALCIUM AMMONIUM NITRATE

Sl. No.	Sample of CAN	Calcium Nitrate Tetrahydrate from graph, %
1	Nangal	1.2
2	Rourkela	1.18

It may be mentioned here that the percentage of calcium nitrate tetrahydrate in both Rourkela and Nangal samples of CAN, as determined by Indian Standard Institution's method of estimation, was found to be 1.1 per cent in both cases.

Acknowledgements

The authors' thanks are due to Sri M. K. Sen for analysing the samples and to Sri Sisir Mukherjee for assistance. Thanks are also due to Dr. K. R. Chakravorty, General Manager of this Division, for his constant encouragement and active support for this work, and also for permission to publish this paper.

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Physical Investigation of Calcium Ammonium Nitrate

By

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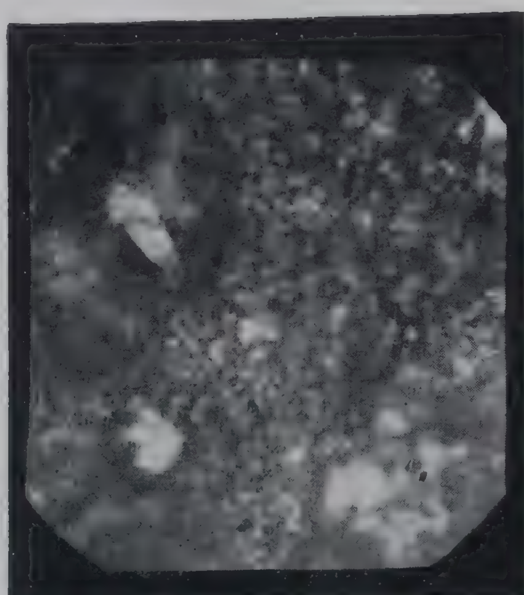
Physical investigation of five different samples of calcium ammonium nitrate (CAN) having similar bulk composition has been made with particular reference to their surface texture and the state of aggregation of their crystalline constituents. It has been observed that there is a distinct variation in the surface texture as well as apparent volume of the caked and uncaked samples, but their D.T.A. thermograms are similar. The transition temperature of NH_4NO_3 IV$\leftarrow\rightarrow$III at 32°C remains unaffected in each case.

Introduction

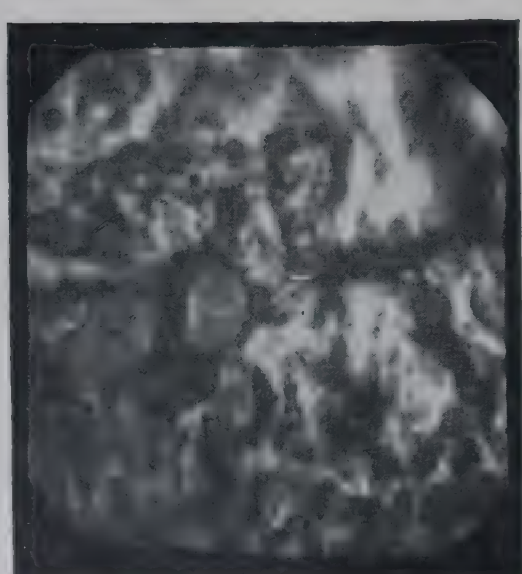
The utility aspect of calcium ammonium nitrate is intrinsically related to its chemical history. If the CAN is caked, its value as a fertilizer diminishes to a great extent. The variables which accelerate the caking process of this fertilizer are the composition, moisture content, time, temperature and the storage conditions, etc. But very little is known of the part played by the other physical characteristics, such as the surface texture, bulk structure, as well as the state of aggregation of the different crystalline constituents on the caking process.

It is well-known that ammonium nitrate, which is the major phase of CAN, constitutes the main nitrogenous base of this fertilizer, while the other predominant constituent viz. limestone is a diluent. The phase transition of NH_4NO_3 at 32°C from type IV$\leftarrow\rightarrow$III, is very prone to caking, because it is possible only in presence of moisture and takes place through solution and a recrystallisation process.[1] Besides their main constituents, quartz, dolomite, talc and calcium nitrate are also present as very minor phases. Of these, calcium nitrate is formed by the action of calcium carbonate on amonium nitrate. It has been observed that ammonium nitrate with calcium nitrate forms a double salt, which does not exhibit polymorophism of ammonium

Fig. 1—Microphotographs Showing Surface Texture of CAN Samples (Magnification 600X).

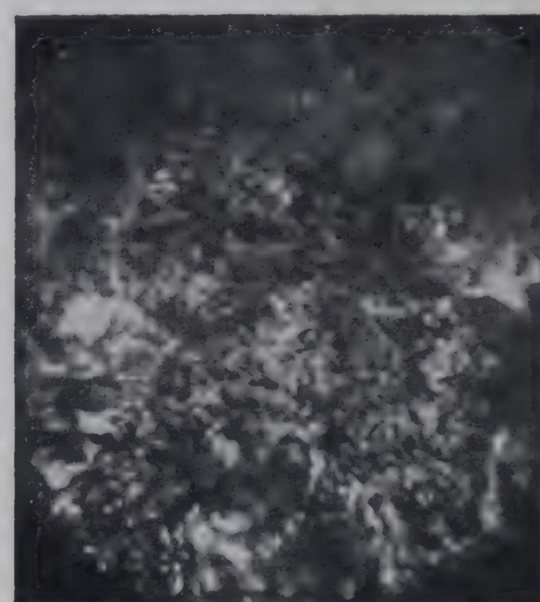


Sample 1



Sample 2

Sample 3



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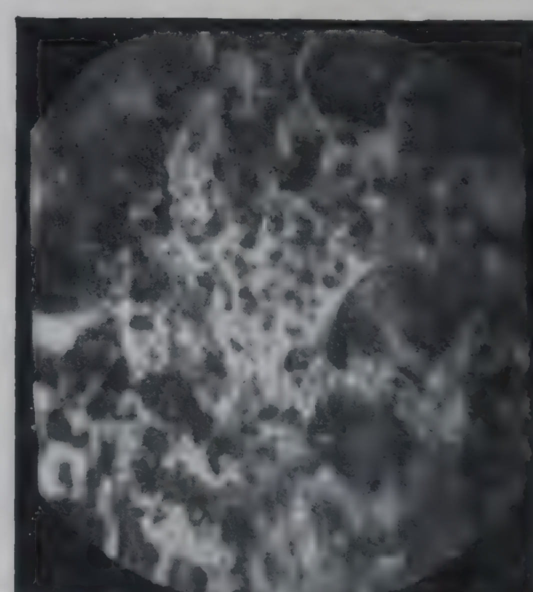

Sample 5

nitrate.[2] It would be, therefore, interesting to study the surface texture as well as the state of aggregation of the different crystalline constituents of some CAN samples which are believed to be related with their caking phenomena.

Experimental

Of the five different samples selected for the present investigation, two were from Nangal and the rest from the Rourkela fertilizer plant. They were designated as sample No. I, II, III, IV & V respectively. These were prepared in the factory by mixing a hot melt of ammonium nitrate containing 6-10 per cent water with ground limestone particles. The materials were then dried when globules were formed. Except the samples II and V, the rest were coated with about 0.3-0.4 per cent finely ground soapstone.

The surface texture of the samples was examined by a polarizing microscope in the reflected light under identical condition using a magnification of 600x (Fig.1).

The moisture content was determined by drying the sample at 105°C, and the apparent volume by the mercury displacement method (Table 1). It is worthwhile to mention here that the standard method of moisture determination is liable to some error due to loss of NH_3, CO_2 etc. at 105°C in the case of present samples.

TABLE 1—Apparent Volume and Moisture Content of CAN

Sample No.	*Apparent Volume, c.c./100 g.*	*Moisture, %*
I	55.40	0.97
II	56.30	1.61
III	55.93	2.88
IV	55.24	2.62
V	55.82	1.88

The differential thermal analysis (D.T.A.) of these samples was performed in a manually operated apparatus fabricated in this laboratory in the range 26°-90°C (Fig. 2). The rate of rise of temperature was 0.5°C/min. up to 40°C and about 2°C/min. afterwards, and thermocouple used was of chromel/alumel. The temperature of furnace was recorded by means of a previously calibrated indicator. The sample holder was made of thin platinum cylinder, and the reference substance used was α-Al_2O_3.

Discussion

An examination of surface texture of different varieties of CAN reveals an interesting feature of their caking phenomena, when examined under a microscope by reflected light (Fig. 1). Except sample IV, the rest shows white zones on their surface. These zones represent areas where moisture is present, but there is a distinct variation in the size of the zones. The size is smallest in the sample I and biggest in III. In case of III, the zones are surrounded by aggregated diluent particles. The surface textures of sample II and V are intermediate between those of I and III, but in case of II the zones are bigger than those of V. In contrast with other samples, the surface of IV is covered uniformly by fine particles. In this case practically no such zones

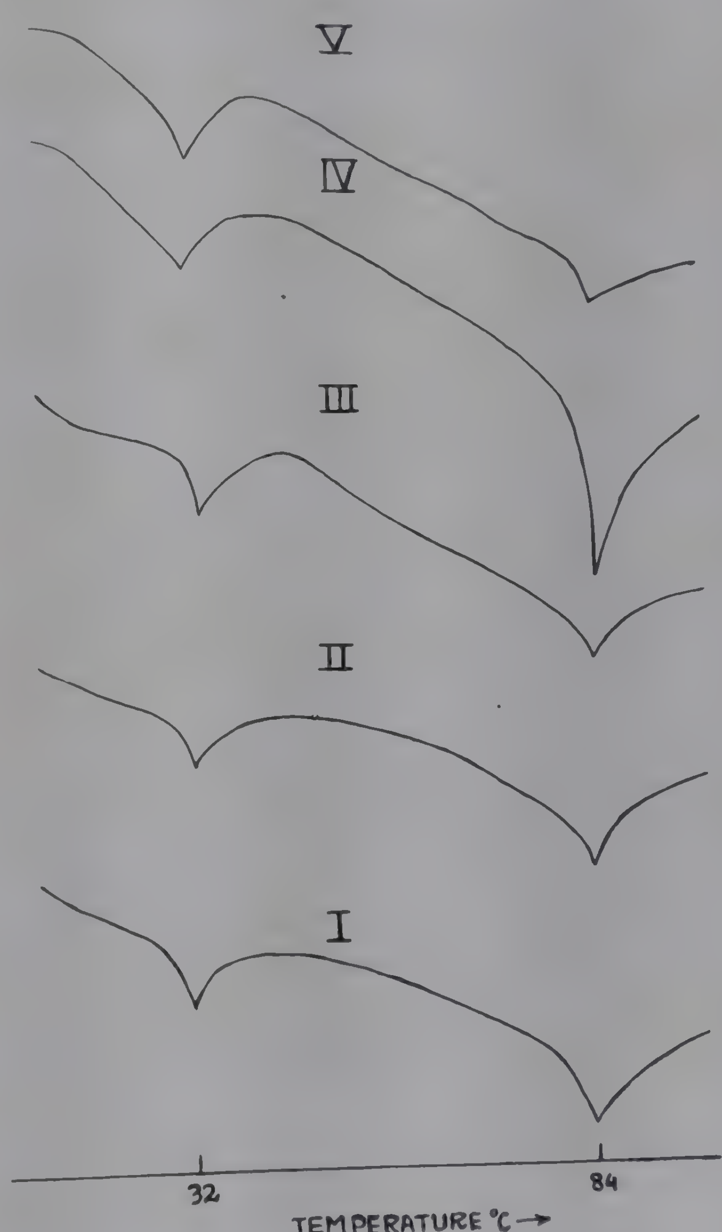

Fig. 2. DTA Thermograms of Different CAN Samples.

have been developed, and there is no aggregation of diluent particles.

Incidentally, it can be remarked that samples IV and I show the least caking, while sample III, which exhibits biggest zones of moisture on its surface among all other samples studied, was found to be the most heavily caked one. Again it has been observed that the size of the above zones increases with increase of the apparent volume of the samples having approximately similar moisture content. This volume is lower in case of IV and V than in III and II, but it is to be noted that IV has the lowest apparent volume, and practically no zones. As compared to sample IV, sample I has a higher apparent volume and a greater area of white zones, although its moisture content is lower.

D.T.A. data reveals that endothermic peaks are present at 32° and 84°C in each case (vide Fig. 2). This observation no doubt unequivocally confirms the presence of free NH_4NO_3 type IV in the system.

It is worth mentioning here that moisture, calcium nitrate, calcium carbonate, dolomite, quartz, as well as coating agent do not affect the characteristic inversion temperature of NH_4NO_3 type IV$\longleftrightarrow$III in these samples.

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Thanks are due to Dr. K. R. Chakravorty, General Manager, P & D Division, for his constant encouragement and kind permission to publish this paper. Thanks are also due to Dr. B. K. Banerjee, and Mr. K. C. Banerjee, both of P & D Division, for their helpful suggestions.

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Removal of Nitrogen from the Fertilizer Factory Effluent by Biochemical Nitrification and Denitrification*

By

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The removal of nitrogen from the effluents of nitrogenous fertilizer works by biochemical nitrifiaction and denitrification has been studied and method has been worked out. A cultural complex of nitrifying bacteria has been developed with the help of which ammoniacal nitrogen upto 2000 ppm. can be oxidized mostly to nitrous and partly to nitric acids by continuous aeration for about 40 hr. The acidity is neutralized by adding magnesium carbonate into the solution for maintaining the pH between 7.2 and 7.8.

The solution containing the oxidized nitrogen is then transferred into another vessel containing mixed cultures of anaerobic microorganisms. After incubation with a layer of groundnut oil on the surface of the solution, the oxidized nitrogen is reduced quickly to elementary nitrogen which escapes to air and is thus lost from the system. It has been observed that a solution containing about 1500 ppm. of nitrite nitrogen can be denitrified in about 20 hr. Thus, a 60 hr. retention period for treatment will be necessary in case the effluent contains about 1500—2000 ppm of ammoniacal nitrogen, while with lesser concentration, the period is considerably reduced.

In the nitrogenous fertilizers industry, a certain amount of inorganic nitrogen finds invariably its way into the factory effluents. As most of the fertilizer factories in India are located far away from the sea and some of the future ones are also likely to be so, the effluents from them will, therefore, invariably be discharged into some of the inland streams. Such effluents generally contain free ammonia, ammonium salts

* Paper to be presented at the Seminar on Wastes & Effluents in Chemical Industries to be held at the Sindri Unit of FCI Ltd.

and sometimes also nitrates, all of which are undesirable in river water beyond a certain concentration; the former two are harmful for normal fish and aquatic vegetation, while the latter in high concentration makes water unfit for potable use.

The elimination of nitrogenous compounds from large bulks of effluents by chemical means is difficult and very expensive. With the projected large-scale expansion of nitrogenous fertilizer industry, the problem of nitrogen removal from industrial effluent for preventing water pollution is assuming greater magnitude. The necessary modification in the manufacturing process might reduce the quantity, but complete removal is not feasible. Hence a study was undertaken to explore the possibilities of removing inorganic nitrogen from such effluents by biochemical means.

There are certain bacteria, known as autotrophic in nature which can synthesize their own food from CO_2 of the air, using energy from the oxidation of some inorganic compounds. Those belonging to the genera of *Nitrosomonas*, *Nitrosococcus*, *Nitrosospira*, *Nitrosocystis* and *Nitrosoglea* can oxidize ammonia to nitrous acid, while others of the genera *Nitrobacter* and *Nitrocystis*, widely present in nature, carry out the oxidation further from nitrous to nitric acid[1-4] and are perhaps the chief agents for natural nitrification.[5]

There are other bacteria in nature, which can survive and also multiply in the absence of oxygen. These may be facultative or obligate anaerobes which can reduce NO_2 or NO_3 to nitrogen. The whole process of nitrification and denitrification can be represented diagramatically (Fig. 1).

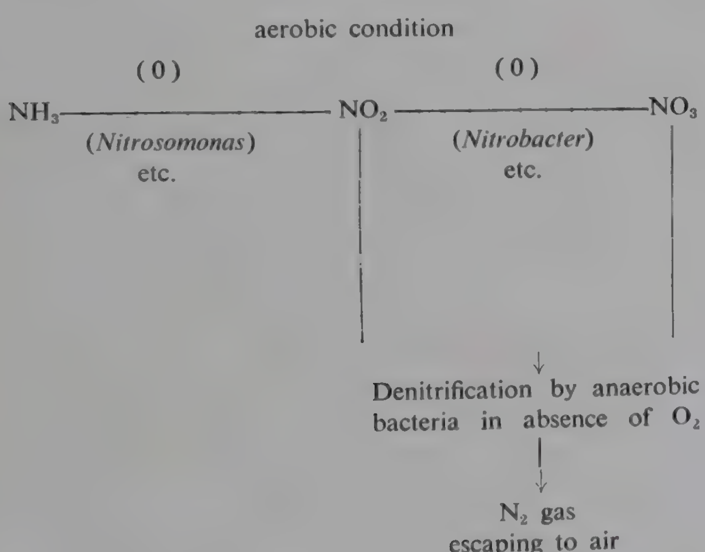

Fig. 1—Oxidation & Reduction of Inorganic Nitrogenous Compounds

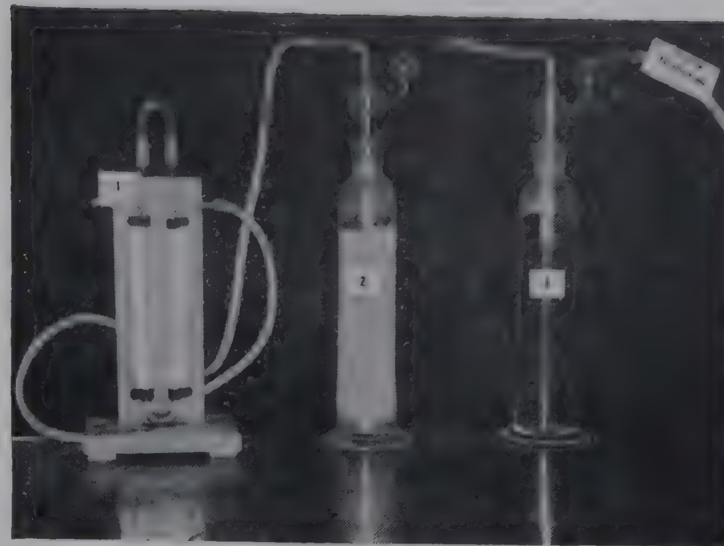

Fig. 2. Oxidation of Ammoniacal Nitrogen.

1. Flowmeter Indicating the Volume of Air Passed.
2. Nitrification Bottle Containing Bacterial Sludge and Nutrient Solution.
3. Bottle Containing dil H_2SO_4 to Absorb NH_3 Released During Aeration.

For effluent treatment, complete oxidation of NH_3 to NO_3 can be avoided, and the nitrite may be directly denitrified as this will involve lesser time of treatment and hence retention time.

Experimental

(*a*) *Development of Cultures for Nitrification:* 1 g. of well-cultivated soil was taken in a gas washing bottle, and 250 ml. of a nutrient solution, containing 0.25 g. of K_2HPO_4, 0.5 g. of NaCl, trace of $FeSO_4$, 0.5 g. of ammonium sulphate and 0.2 g. of $MgSO_4$, was added. Air was bubbled through the bottle at the rate of 0.8 to 0.9 cft./hr, and ammoniacal as well as oxidized nitrogen were then estimated at regular intervals by Kjeldahl method (Fig. 2). At the end of 3 to 4 weeks, the first sign of nitrification was noted, and its rate then increased steadily. The changes of pH were very rapid during this period and sufficient amount of magnesium carbonate was added in order to keep the pH of the solution between 7.2 and 7.8. As soon as the nitrification was complete, the supernatant liquid was decanted off and fresh nutrient solution was added, and aeration continued. The process was repeated several times until the culture was very active as evidenced by the rate of nitrification. In preparing a solution containing different concentrations of ammoniacal nitrogen for nitrification studies, fertilizer grade ammonium sulphate was used.

(*b*) *Development of Cultures for Denitrification:* Garden soils and partially decomposed cow dung were

mixed in equal proportion and incubated in pots for a month. 100 g. of the resulting compost (60.5 g. dry wt.) was taken in 3-l. flasks to which a nutrient solution—comprising magnesium nitrate, 1 g., K_2HPO_4 2 g., sucrose, 1 g. and tap water 1000 ml, was added up to the neck. The liquid surface in flask was then covered with a layer of groundnut oil to prevent any access of air, and the contents incubated at room temperature. Nitrate nitrogen of the solution was then estimated at regular intervals. Denitrification was very slow initially, but at the end of about 45 days most of the nitrogen in the solution was lost. The supernatant liquid was then decanted off and fresh solution containing magnesium nitrate was again added. The whole process was repeated several times till the rate of denitrification was appreciable. The activated compost (inoculum) was collected from the bottom of the flask and stored. Whenever required for experiments, the inoculum compost was diluted properly and 20 ml. of the resulting slurry yielding 5 g. of dry matter was then taken in 250 ml. flasks to which sufficient solution was added to make the total volume 250 ml. Initial sample was taken after half an hour giving sufficient time for uniform distribution of the soluble matter.

Results and Discussion

(1) *Nitrification:* It may be noted from Tables 1 and 2 that the total nitrogen obtained after nitrification is always less than that of initial—ammoniacal as well as oxidized—nitrogen taken. It is evident from Table 1 that the loss, though its extent varied considerably in different experiments employing same concentrations, increased with the increase of the initial concentration of ammoniacal nitrogen used. This loss is mostly due to the escape of ammonia and decomposition of a part of nitrites during oxidation. The extent of ammonia, lost in the process, has been estimated (Table 1). A smaller fraction, of course, has been consumed by the organisms and converted into organic form.

TABLE 1—BIOCHEMICAL OXIDATION OF AMMONIACAL NITROGEN

(Nitrogen After 40 Hr. Aeration, ppm)

Initial Conc.		*Final Conc.*		*Loss of Nitrogen*	
Ammoniacal Nitrogen	*Oxidized N_2*	*Ammoniacal Nitrogen*	*Oxidized N_2*	*Total*	*Loss as NH_3*
198.3	10.3	5.2	162.1	41.3	27.8
342.5	30.9	5.2	302.1	66.1	48.2
749.3	25.8	7.7	677.3	90.1	76.0
1434.3	113.3	23.2	1359.5	164.9	105.3

It is also observed that the conversion of ammoniacal nitrogen to an oxidized form is almost complete in 40 hours for the initial concentrations studied. viz. 198.3 to 1434.3 ppm, of ammoniacal nitrogen. The possibility of still quicker rate of nitrification was examined in further experiments (Table 2), and it has been noted that efficient nitrification may be obtained in about 20 hours if the initial concentration of ammoniacal nitrogen in solution is about 500 ppm or less. For higher concentrations ranging from 1000 to 2000 ppm, aeration for 40 hours seems to be the minimum requirement. An inhibitory effect is noted when too high a concentration, viz. 2793.6 ppm, of ammoniacal nitrogen is used as the amount of oxidized nitrogen obtained even after 40 hours aeration is only 570.3 ppm (treatment e, Table 2).

TABLE 2—BIOCHEMICAL OXIDATION OF AMMONIACAL NITROGEN

(Nitrogen after Continuous Aeration, ppm)

		Time of Incubation, hr.					
	0 *Initial Conc. of N_2*	15	20	25	30	35	40
(a) Ammonia N_2	513.9	296.0	27.8				
Oxidized N_2	29.2	180.0	439.9				
(b) Ammonia N_2	1080.4			661.5	485.4	157.6	5.8
Oxidized N_2	5.8			315.3	434.6	743.1	886.6
(c) Ammonia N_2	1565.5				786.6	375.2	5.8
Oxidized N_2	81.7				706.6	1089.4	1398.9
(d) Ammonia N_2	2019.5				1181.3	600.3	133.8
Oxidized N_2	34.9				605.3	1000.3	1423.0
(e) Ammonia N_2	2793.6						1695.7
Oxidized N_2	34.9						570.3

(2) *Denitrification:* The time required for complete denitrification was studied experimentally and it has been observed that the losses of nitrate nitrogen during 24 hours are 231.7, 463.3 and 493.9 ppm in cases of initial concentrations of 283.2, 566.5 and 1169.0 ppm respectively (Table 3).

TABLE 3—DENITRIFICATION OF NITRATE SOLUTION

[Nitrate-Nitrogen, ppm.]

Initial Conc.	Loss in 24 Hr.		Loss in 30 Hr.	
	Total Loss	% loss	Total Loss	% loss
283.2	231.7	81.8	259.9	91.8
566.5	463.3	81.8	507.2	89.5
1169.0	493.9	42.2	1068.5	91.4

Thus with the amount of inoculum—20 ml. slurry containing 5 g. dry matter—initially supplied, 231.7 to 493.9 ppm of nitrate nitrogen can be denitrified within 24 hours, a greater loss being noted from solutions containing higher concentrations of nitrogen. With two lower concentrations, this means about 82 per cent removal of nitrogen, but the corresponding figure for the highest concentration of nitrogen employed is only 42.2 per cent. This is probably due to the lesser number of bacterial units present than what is necessary for denitrification of such a high concentration of nitrate solution. The bacteria, however, multiply quickly, and the number of active units soon increase resulting in a quicker rate of denitrification during next few hours, as is evident from data obtained after 30 hours incubation. Here, about 90 per cent denitrification has been achieved in all concentrations used. It is evident, therefore, that the rate of denitrification is dependent upon the concentration of nitrate nitrogen used and the number of active bacterial cells present at a time under the conditions of the present experiment. If a higher concentration of nitrogen is employed, the greater number of bacterial cells will have to be added either initially, or sufficient time must be allowed for the multiplication of the existing cells so that the desired number of active units may come forth. Under the present experimental conditions, the required number of bacterial cells are attained during 24 to 30 hours, and as a result the rate of denitrification has been hastened up during this period.

It has been noted in nitrification studies described earlier, that the oxidized nitrogen obtained after 40 hours aeration consists mainly of nitrite. In the denitrification process therefore, the nitrite is likely to be reduced quicker than the nitrate in solution. Experiments were therefore carried out with solution from nitrification vessels containing oxidized nitrogen, mostly nitrite, and with the quantity of nutrients noted earlier.

TABLE 4—DENITRIFICATION OF SOLUTION CONTAINING OXIDIZED NITROGEN FROM NITRIFICATION VESSELS

Sl. No.	Treatment	Oxidized Nitrogen, ppm. Time of Incubation, hr. 0	15	20
1.	Solution from Nitrification bottle-Control	659.2	255.8	138.7
2.	Solution 1+ 0.05% K_2HPO_4	638.6	271.9	138.7
3.	Solution 1+ 0.5% Sucrose	612.8	11.1	0.0
4.	Solution 1+ 0.05% K_2HPO_4+ 0.5% Sucrose	638.2	11.1	0.0

It is evident from Table 4 that the removal of oxidized nitrogen (viz. treatments 3 and 4) is more than 98 per cent in 15 hours but is complete in 20 hours. This is expected as this solution contained nitrogen mostly in the form of nitrite and hence easily reducible. This is definitely a marked improvement of the time required for denitrification of nitrate solution as noted earlier (Table 3).

It has been also observed that the addition of sucrose alone is sufficient for the nutrient requirement, and further supply of phosphate seems to be unnecessary (Table 4). The optimum requirement of sucrose for denitrification was further studied (Table 5). It has been noted that a minimum concentration of 0.2 per cent of sucrose in solution is necessary for proper denitrification, and further increase in its concentration does not hasten up the process.

TABLE 5—DENITRIFICATION OF OXIDIZED NITROGEN

Sl. No.	Treatment	Oxidized Nitrogen, ppm. Time of Incubation, hr. 0	10	15	20
1.	Solution from Nitrification Vessels—Control	892.3	573.5	560.3	558.2
2.	Solution 1+0.1% Sucrose	895.3	305.8	211.5	205.5
3.	Solution 1+0.2% Sucrose	873.5	225.1	13.2	7.2
4.	Solution 1+0.4% Sucrose	888.5	221.3	13.5	5.2

In earlier experiments with nitrate nitrogen 0.5 per cent sucrose was used in solution and this concentration was found to be the optimum. Hence a reduction

of sucrose requirement for denitrification of nitrite nitrogen obtained from nitrification of ammonium sulphate is notable. This is probably due to the enrichment of the solution with respect to soluble carbohydrate. as the organisms involved are autotrophic and can fix up atmospheric CO_2.

That the denitrification of solution containing nitrite was a purely bacterial reduction was confirmed experimentally (Table 6). The flasks containing (1) No inoculum-control, (2) sterilized inoculum, and (3) active compost-inoculum, were filled with sodium nitrite solution containing 0.4 per cent sucrose and 0.05 per cent K_2HPO_4, maintaining anaerobic conditions by a layer of groundnut oil on the liquid surface.

It is evident that the loss of nitrogen from nitrite solution under anaerobic conditions is neglibible in absence of the proper bacteria (Table 6, treatments 1 and 2), while its presence (as in treatment 3) has effected removal of 1233.9 and 1432.9 ppm of nitrogen from the solution in 15 and 20 hr. respectively. Similar results have also been noted with oxidized nitrogen obtained from nitrification experiments.

TABLE 6—DENITRIFICATION OF NITRITE SOLUTION IN PRESENCE OF ANAEROBIC MICROORGANISMS

Sl. No.	Treatment	Nitrogen, ppm — Time of Incubation, hr. 0		15		20	
		A*	B†	A	B	A	B
1.	Nutrient Soln. No Inoculum Added. Control	88.8	1533.0	88.2	1482.9	88.2	1480.8
2.	Nutrient Soln.+Sterilized Inoculum	69.3	1505.7	69.3	1467.9	69.3	1466.9
3.	Nutrient Soln. +Inoculum Compost	31.5	1530.0	31.5	296.1	31.5	97.1

*A=Ammoniacal nitrogen
†B=Nitrite nitrogen

Conclusion

The removal of inorganic nitrogen by nitrification and denitrification employing mixed cultures of microorganisms, developed in this laboratory, involves two stages. Firstly, all ammoniacal nitrogen is oxidized mostly to nitrite in 40 hr. of aeration by autotrophic bacteria (like *Nitrosomonas* etc.) under perfectly aerobic and other suitable conditions. If aeration is prolonged, nitrite is further oxidized to nitrate (by *Nitrobacter* etc.) also present in mixed culture. Secondly, the oxidized nitrogen in aqueous solution, when incubated under anaerobic conditions in presence of a host of facultative and obligate anaerobic bacteria, is reduced to elementary nitrogen. This being an inert gas, escapes to the atmosphere and is thus removed from the system.

It is apparent that a solution containing ammoniacal nitrogen even as high as 1565 ppm could be oxidized in about 40 hr. under aerobic conditions. The solution thus obtained from the nitrification process could then be denitrified under anaerobic condition in about 20 hr. Thus, by a retention period of about 60 hr., effluent containing about 1500 ppm of ammoniacal nitrogen could be relieved of its nitrogen content. The retention time may be less if the ammoniacal nitrogen content of the effluent is lower. Some of the effluent of nitrogenous fertilizer factories are likely to contain as high as 1500 ppm of ammoniacal nitrogen and hence the removal of the same from the effluent by this method seems to be quite practicable.

It has been noted that if a very high concentration of ammoniacal nitrogen of about 2800 ppm is employed, the rate of nitrification is considerably slowed down. But the cultural complex soon regains its original rate within a few days if the concentration of ammoniacal nitrogen is brought down to 1000 to 1500 ppm.

The results reported here were obtained by using solutions containing ammonium sulphate prepared in this laboratory. Further studies are now being carried out with the actual effluent as discharged by the Sindri Fertilizer Factory and the results will be reported in due course.

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Trivalent Arsenic Compound as an Inhibitor of Corrosion of Stainless Steel in Sulphuric Acid

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Weight-loss experiments carried out with 18-8 stainless steel in boiling solutions of sulphuric acid (0.3 g./100 ml.) and varying amounts of chloride both in presence and absence of different concentrations of a trivalent arsenic compound have shown that the latter is a very efficient corrosion inhibitor. A pronounced cathodic shift in potential of stainless steel in the acid solution is observed in presence of trivalent arsenic. The mechanism of inhibitor action has been explained by assuming the formation of a chemisorptive bond between the trivalent arsenic compound and the metal atom.

Introduction

In the manufacture of ammonium sulphate by the gypsum process, the free acidity of the evaporator liquor is usually kept at 0.2—0.3 g./100 ml. of sulphuric acid. Boiling ammonium sulphate solutions having this level of acidity are corrosive to stainless steel evaporators. To inhibit such corrosion trivalent arsenic has been used. The present investigations were undertaken to study the action of the inhibitor in preventing corrosion of stainless steel in sulphuric acid under different conditions as the necessary data were not available. In particular, it was thought desirable to study the action of this inhibitor in presence of different concentrations of chloride ion which is known to aggravate corrosion of stainless steel.

In the first phase of the work, weight-loss experiments were carried out with stainless steel in boiling solutions containing 0.3 g./100 ml. of sulphuric acid and different amounts of trivalent arsenic, both in presence and absence of chloride. Further, to study the action of the inhibitor in presence of high concentrations of chloride, experiments were carried out by keeping definite concentrations of the trivalent arsenic, viz. 0.5 g./100 ml. and 1 g./100 ml. of arsenious oxide, in the acid solution and increasing the chloride concentration up to 10g./100 ml. of sodium chloride. To elucidate the mechanism of the action of inhititor under such conditions, the electrode potentials of stainless steel were determined in the boiling acid solutions containing different amounts of trivalent arsenic and chloride.

Experimental

Materials: Titanium stabilised 18-8 stainless steel sheet 1/8″ thick of brand SF-22 (manufactured by Messrs. Samuel Fox & Co.) was used. Sulphuric acid (E. Merck), arsenious oxide (E. Merck) and sodium chloride (B.D.H.) used in these experiments were of the analytical reagent grade. In all experiments, a sulphuric acid concentration of 0.3 g./100 ml. was maintained in the test solutions, and the trivalent arsenic was added in the form of a strong solution of arsenious oxide in caustic soda. Measured volumes of this solution of known concentration were added to solutions containing more than the desired amount of sulphuric acid; the strengths were then adjusted so that the final test solutions contained 0.3 g./100 ml. of sulphuric acid.

Weight-Loss Experiments: Reactangular test specimens, approximately 30 sq. cm. in surface area, were sheared from stainless steel sheets and a hole was drilled in each of them. The surfaces of the specimens were prepared by No. 0 emery paper and the surface area was measured accurately with callipers. The coupons were then degreased in boiling toluene, washed with absolute alcohol, dried by blowing hot air over them and kept in desiccators for seven days before use. They were suspended from glass hooks in the boiling test solutions (*c* 400 ml.) kept in 500 ml. Erlenmeyer flasks fitted with a reflux condenser. The specimens were introduced into the boiling solutions instead of first placing them in cold solutions and then raising the

latter to boil. This procedure was necessary since corrosion rates were found to be low and erratic when the specimens were first placed in the cold solution. Seligman[1] has also reported similar behaviour of stainless steel in acid solutions. The cupons were kept in the test solutions for 8 hours and then taken out, washed with water, and the cleaning and drying processes were repeated. The weights of the coupons were noted before and after the experiments. The weight losses were recorded as mg./sq. dm./day. Two or more experiments were carried out under each set of conditions and the averages taken.

Potential Measurements: For potential measurements in the boiling solutions, a modified form of the apparatus, described by Streicher[2], was used. The stainless steel electrode was placed in the boiling acid solution kept in a 500 ml. Erlenmeyer flask fitted with a reflux condenser. A wire of the same composition as that of the electrode was fixed to the latter and was taken through the reflux condenser and connected to a potentiometer. A glass tube, with a porous sintered glass plate fused inside it, was sealed itno the lower portion of the Erlenmeyer flask and formed the side arm. The side arm was filled with the same solution as in the flask and was kept cold by a glass jacket through which water was circulated. The liquor in the side-arm was in contact with the same solution kept in a small beaker, and the latter solution was ultimately in connection with the saturated calomel electrode. Potential measurements were carried out with a potentiometer†.

All the potential values reported here are those which were noted after 8 hr. by which time the potential became steady. The values were reproducible within 10 mv., and do not include corrections for junction potential and temperature.

Results and Discussions

In the uninhibited acid, stainless steel corroded at high rates, namely 1810 and 2123 mg./sq.dm./day respectively in presence and absence of 0.2 g./100 ml of sodium chloride; the corresponding potentials with respect to saturated calomel electrode (s.c.e.) were −466 and −460 mv. respectively (Table 1). The corrosion rates were reduced to very low values, namely 6.3 and 5.8 mg./sq.dm./day, with an inhibitor concentration of 0.06 g./100 ml. of arsenious oxide in the solution. At concentrations of 0.2 g./100 ml. of sodium chloride and 0.04 g./100 ml. of arsenious oxide, the corrosion rates were still high, although they were less

† manufactured by Pye Ltd., Cambridge, U.K., (Catalogue no. 7569P).

TABLE 1—CORROSION AND INHIBITION OF STAINLESS STEEL IN BOILING DILUTE SULPHURIC ACID (0.3 g/100 ml) IN PRESENCE AND ABSENCE OF TRIVALENT ARSENIC AND CHLORIDE

		With NaCl 0.2 g./100 ml.		*Without NaCl*	
Sl. No.	*Concentration of As_2O_3 g./100 ml.*	*Corrosion Rate, mg./sq. dm./day*	*Potential vs s.c.e., mv*	*Corrosion Rate, mg./sq. dm./day*	*Potential vs s.c.e., mv*
1	None	1810	−466	2123	−460
2	0.02	584	−461	1294	−460
3	0.04	438	−433	471	−472
4	0.06	6.3	−300	5.8	−282
5	0.08	5.1	−255	5.2	−243
6	0.10	4.0	−254	3.7	−220
7	0.15	3.6	−239	3.5	−204
8	0.20	2.9	−228	3.5	−185
9	0.25	2.9	−173	3.4	−183
10	0.30	3.1	−136	3.0	−132
11	1.0	1.9	+167	2.1	+ 81
12	2.0	2.0	+162	1.9	+126
13	4.0	2.2	+161	2.1	+122

than those in the uninhibited acid. The corrosion rate of about 6 mg./sq. dm./day corresponds to very effective inhibition, and on further increasing the concentration even up to 4 g./100 ml. of arsenious oxide the rate is reduced to only 2 mg./sq. dm./day. By keeping an inhibitor concentration of 1 g. As_2O_3/100 ml. in the solution and gradually increasing the amounts of chloride, the effective inhibition was obtained even with a chloride concentration as high as 10 g./100 ml. (Table 2). With a lower concentration of trivalent arsenic, viz. 0.5 g./100 ml. of As_2O_3, inhibition was only slightly less effective at higher levels of chloride in solution. These results show that the trivalent arsenic is an efficient corrosion inhibitor of stainless steel in dilute sulphuric acid, even in high concentration of chloride.

The potential becomes more noble in the presence of trivalent arsenic and there is an increasing shift in the cathodic direction with an increase in arsenite concentration. At a concentration of 2 g./100 ml. of As_2O_3 in the acid solution with no chloride, the total cathodic shift in potential is 586 mv; further increase in As_2O_3 concentration does not make any appreciable change in the potential. Similarly, in the solution containing 0.2 g./100 ml. of sodium chloride and 1 g./100 ml. of As_2O_3 the actual potential was +167 mv. and the cathodic shift in potential reached a value of 633 mv. By keeping this concentration of arsenious oxide (1g. /100 ml.) constant and gradually increasing the

TABLE 2—EFFECT OF TRIVALENT ARSENIC AS INHIBITOR IN PRESENCE OF INCREASING AMOUNTS OF CHLORIDE
(As_2O_3 concentrations 0.5g./100 ml. & 1g./100 ml. in Boiling Dilute H_2SO_4 (0.3g./100 ml.))

Sl. No.	Concentration of NaCl g./100 ml.	Solutions with 0.5g./100 ml. of As_2O_3		Solutions with 1g./100 ml. of As_2O_3	
		Corrosion Rate of Stainless Steel, mg./sq.dm./day	Potential of Stainless Steel, vs s.c.e. jmv	Corrosion Rate of Stainless Steel, mg./sq.dm./day	Potential of Stainless Steel, vs s.c.e. jmv.
1	0.2	3.0	− 70	1.9	+167
2	0.3	3.2	−132	2.3	+168
3	0.4	3.0	−197	2.7	+109
4	0.5	3.9	−217	2.6	+ 95
5	0.6	3.9	−224	—	—
6	0.7	5.6	−230	—	—
7	0.8	—	—	3.0	+ 15
8	0.9	—	—	2.5	− 48
9	1.0	—	—	3.0	− 53
10	1.5	—	—	3.0	− 83
11	2.0	8.6	−243	3.0	− 90
12	2.5	—	—	3.5	−110
13	3.0	10.4	−245	4.8	−160
14	5.0	12.4	−268	5.2	−209
15	10.0	14.2	−318	5.6	−235

amounts of chloride, it was found (Table 2) that the potentials were shifted more and more in the anodic direction and at a concentration of 10 gm./100 ml. of sodium chloride the potential became −235 mv. The corrosion rate was, however, very low under these conditions. With a lower concentration of trivalent arsenic, namely 0.5 g./100 ml. of arsenious oxide a potential of −230 mv. was attained with a chloride concentration of 0.7 g./100 ml. of sodium chloride and with a concentration of 10 g./100 ml. of sodium chloride the potential became −318 mv., the corresponding corrosion rate being 14.2 mg./sq. dm./day. From the results (Tables 1 & 2), it, therefore, appears that the electrode potential of stainless steel in dilute sulphuric acid must reach a certain value in the *anodic* direction before appreciable corrosion sets in. This value seems to be more negative than −300 mv. with respect to saturated calomel electrode, (s.c.e.) in the present series of investigations.

The high values of cathodic shift in potential in presence of trivalent arsenic show that the latter is behaving as an anodic inhibitor[3] in the present case (Table 1). The inhibitor was commonly supposed to be a cathodic[3-5] one in acid solutions. However, in an earlier publication[6] it was shown that trivalent arsenic in acid solution inhibits both cathodic and anodic reactions on mild steel with the anodic effect slightly predominating. Corrosion inhibition with trivalent arsenic particularly at the elevated temperature, is, however, much less effective in case of mild steel than in the case of stainless steel. This inhibitor in suitable doses almost completely eliminates corrosion in boiling solutions of sulphuric acid (0.3 g./100 ml.) even in presence of considerable amounts of chloride. This effective inhibition of corrosion by trivalent arsenic coupled with the pronounced cathodic shift in potential suggests a strong chemisorption of this substance, specially at the anodic sites of the metal. This is in line with the views of several investigators on the action of other effective inhibitors. Hackerman[7-9] et al postulated preferential chemisorption at anodic sites to explain the inhibition of corrosion and cathodic shift in potential with organic inhibitors of corrosion of mild steel in acid solutions. Such a mechanism of adsorption has also been assumed by Cartledge[10] to explain the inhibitive action of inorganic inhibitors. Anoschenko[11] and Balezin[12] et al point out that adsorption of the inhibitor, inorganic or organic, on the metal should be assumed to explain its action and that for a strong inhibitive effect, chemisorption of the inhibitor or the formation of an insoluble chemical compound on the surface of the metal should be assumed.

The chemisorption mechanism for the action of trivalent arsenic in inhibiting corrosion of stainless steel in acid solution seems to be supported by its efficacy even in presence of a high concentration of chloride. The adverse effect of chloride ions on the corrosion resistance of stainless steel has been ascribed by Uhlig[13] to the preferential adsorption of chloride ions on the anodic sites of the metal with the subsequent dissolution of the latter due to the high rate of formation of metal-chlorine bond. The inhibiting action of trivalent arsenic in presence of chlorides can be readily explained as due to its strong chemisorption on the anodic sites of the metal in preference to the chloride ions. A strong chemisorption of trivalent arsenic on the metal would correspond to the formation of a dative bond between the metal and the inhibitor ion by the sharing of a pair of electrons. Maxted[14,15] has pointed out that compounds of group VA & VIB elements* in which atoms contain free electron pairs in the valency shell behave as catalyst poisons particularly towards the transitional elements, the toxicity being due to the power of forming a relatively strong chemisorptive bond with the metal. The bond may be

* in the periodic classification

formed by entry of the electrons from the inhibitor to the d-band of the absorbing metal to give a co-ordinate link, and thereby eliminating any electron deficiencies or holes in the d-band of the metal. The toxicity disappears when the normally toxic element is present in a compound in such a way that it is in a shielded form, that is in a form having a completely shared orbit. Arsenic—a group VA element—has a lone pair of electrons in the arsenious acid[16] ($H_3 AsO_3$) or meta-arsenious acid ($HAsO_2$) or the anions derived from these, as shown below. These are the species supposed to be present mainly in dilute hydrochloric or sulphuric acid[17-19] when arsenious oxide or alkali arsenite is dissolved in the solvent.

Arsenious acid   Meta-arsenious acid

It is, therefore, very likely that the same mechanism, namely strong chemisorption at the anodic sites, is responsible for the action of a substance like trivalent arsenic both as an inhibitor and as a catalyst poison. Such a parellelism between inhibition and poisoning of catalysts has also been put forward by Hackerman[7] and Balezin[12] et al. The formation of a strong chemisorptive bond at the anodic sites of stainless steel by the donation of a pair of electrons from the trivalent arsenic compound would explain the inhibition of the dissolution of the metal as ions and also the cathodic shift in potential due to the reduction of effective anodic areas on the metal.

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Extraction and Estimation of Humic and Fulvic Acids from Soil and their Fractionation by Paper Chromatography

By

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Humic acids sample has been extracted from soil using mild sodium hydroxide and freed from carbohydrates and other sugars using ion-exchange column. The sample has been analysed to ascertain its fundamental components by paper chromatographic technique. The total number of components in both the organic solvent soluble and organic solvent insoluble fractions of humic acids have been found to be eight in n-propanol formic acid: water, and seven in isopropanol: ammonium hydroxide: water systems respectively, using bromo-cresol green as location reagent. The same solvents yield three to four components in fulvic acids. The results have been compared and checked with a sample of humic acids obtained from Switzerland.

The organic matter content of the soil affects to a great extent the efficiency of chemical fertilizers and influences the rate of nitrification. Different constituents of soil humic acids are known to form complexes with them e.g. urea forms an addition complex in presence of water[1]. The soil humic acids have, therefore, been investigated by a number of workers, and the exact number of components of this and fulvic acids are yet the subject of much controversy. Due to high capacity of resolution and sensitivity to traces, chromatographic techniques have been recently applied in determining the components of complex substances like humic acids. Hayashi[2] in his studies on column and paper chromatographic separation of humic acids has reported the presence of three to four bands visible in the ultraviolet light. Trojanwaski[3] in his extraction of humic acids without the use of sodium hydroxide has shown the existence of two types of humic acids, classified on the basis of molecular weight, as α and β fractions. He resolved each fraction into two components having well-defined R_f values. More significantly, the component of smaller molecular weight has lower R_f value than β fraction. Sharpenseel[4] and Kononova[5] have indicated the presence of only two zones visible in day as well as in u.v. light. Singh[6] and co-workers have reported the presence of only two components of humic acids from at least five soil samples of India. Sowden[7], in his work on the fractionation of fulvic acids extracted from B-horizon with perchloric acid and potassium hydroxide, has reported the existence of five fractions as eluted on a cellulose column but expressed his doubt about a clear difference between these fractions.

The pH indicators have been successfully tried with the solvent systems[8] and as a spray reagent[6] in determining the components of organic acids. However, the use of bromo-cresol green seems to have been less investigated and does not seem to have been reported so far in the identification of humic and fulvic acids component. In view of the importance and lack of conclusive data regarding the presence of the different constituents of soil organic matter content in general and in humic and fulvic acids in particular, it was thought desirable to undertake investigation of their components from the Indian soil using bromocresol green as location reagent.

Experimental

The soil was collected from a local farm from the surface up to six inches depth and had uniformly reddish-brown colour with 2.61 per cent average organic matter content and pH 6.70.

Extraction of Humic and Fulvic Acids

500 g. of the soil was treated with 0.1 N hydro-

chloric acid overnight to decompose carbonates etc. and was then repeatedly extracted with 1.5 N sodium hydroxide on water-bath till the extract became faint brown in colour. The dark-brown extract was centrifuged and the clear extract was precipitated with slow addition of dil. hydrochloric acid. The precipitate obtained at higher pH up to 7.5 was filtered and the pH of the filtrate was lowered till further precipitation took place at pH 2.5. The precipitate was allowed to settle and was filtered. The pH of the filtrate was then varied from 0.5 to 13.0 with hydrochloric acid and sodium hydroxide with no further change. Finally the fulvic acids were precipitated from the acidified filtrate by the method of Vissar[9]. A complete extraction procedure is given below (flow diagram).

Purification

(*a*) *Humic Acids:* For further purification of crude humic acids the precipitate was refluxed with 50 c.c. benzene (A.R.) and then in a mixture of acetone+ethanol (1: 1 v/v) for 1 hr. A substantial amount of humic acids was extracted by latter while it remained unaffected with benzene. The insoluble portion was dissolved in 0.1 N. sodium hydroxide and then desalted in multiple stages by batch process with calculated quantities of Dowex 50W-X8 in hydrogen form. Desalting in the column with Dowex 50W-X8 was not possible because the liberated acid lowered the pH to such an extent that it caused precipitation of humic acids in the column. By batch treatment, the pH was lowered to 3.0 to maintain humic acids in solution. After repeating the process twice the solution was filtered and the pH of the filtrate was further lowered by addition of 0.1 N, hydrochloric acid, and humic acids were precipitated at pH 2.5. The precipitate was filtered through Whatman No. 52 filter paper, washed with 1 per cent hydrochloric acid and finally with distilled water. After desalting on Dowex-50W the humic acids substantially dissolved in methanol. The methanol as well as acetone+alcohol soluble fractions were evaporated and the residue

Soil+0.1 N. HCl
↓ Decanted
Treated Soil+1.5 N. NaOH; extracted on water bath;
extract+HCl and filtered

↓ Precipitate: light brown, turns like chalk on washing with water; insoluble in cold acid and alkali; washed with water
- ↓ Precipitate
- ↓ Washing (A)
  - ↓ Dark-Brown Precipitate; soluble in 0.1 N NaOH (B) (Humic acids)

↓ Filtrate at pH 7.5+washing (A)
| Added HCl slowly upto pH 2.5 and filtered.
- ↓ Filtrate: pH 2.5
  | The pH varied from 0.5 to 13.0 and finally fulvic acids precipitated with slow addition of saturated $Ba(OH)_2$ & filtered
  - ↓ Precipitate: Ba-Salts of fulvic acids and humic acids
    | Dissolved in Conc. HCl in cold and filtered
    - ↓ Precipitate: Ba-Humate
      | Dissolved in 1 N/.NaOH, added dil. HCl and filtered
      - ↓ Precipitate: humic acids. Dissolved in NaOH and mixed with (B); added 1.0 N.HCl and filtered
        - ↓ Precipitate: Dark-brown (Humic acids)
        - ↓ Filtrate (colourless rejected)
      - ↓ Filtrate (C)
    - ↓ Filtrate: fulvic acids+(C)
      | added $Ba(OH)_2$ and filtered
      - ↓ Precipitate fulvic acids-Ba-salt
        | Dissolved in 0.2 N.HCl precipitated with $Ba(OH_2)$ and filtered
        - ↓ Precipitate (Fulvic acids-Ba-Salt)
        - ↓ Filtrate (rejected)
      - ↓ Filtrate (colourless; rejected).
  - ↓ Filtrate: light yellow colour, pH 8.5 (rejected)

was kept as humic acids organic solvent-soluble HA (O. S. S.) fraction for analysis. The methanol-insoluble portion was again dissolved in 0.1 N. sodium hydroxide and passed through different columns packed with strongly anion-exchanger Dowex 1-X8 of 80 to 200 mesh (B. S.) in acetate and formate form to remove uronic acids and oligosaccharides. A notable adsorption was observed on the column 0.85 cm.x 8 cm. size in acetate form. The humic acids were reprecipitated from clear dark-brown eluate by the addition of 0.1 N. hydrochloric acid at pH 2.5 and filtered, dried at 40°C for 16 hr. in chromatographic oven and kept as humic acids organic solvent-insoluble HA (O.S.I.) fraction.

(*b*) *Fulvic Acids:* The crude fulvic acids after dissolving in least quantity of 5 N. hydrochloric acid were adsorbed on active charcoal after preheating to 90°C. The desorption of fulvic acids was accomplished with 0.5 N. sodium hydroxide with slight warming. The extract was filtered through Whatman No. 52 filter paper, and the clear deep red-brown filtrate was acidified with hydrochloric acid up to pH 0.5; fulvic acids were then precipitated at pH 6.4 by addition of barium hydroxide. The precipitate was dried overnight at 40°C and extracted separately with a mixture of (i) Benzene+ethanol (1:1 v/v) and (ii) Acetone+ethanol (1:1 v/v) and finally washed with methanol and water. Fulvic acids remained unaffected in these solvents. Further purification was carried out by dissolving it in 20 c.c. of 0.1 N. sodium hydroxide and passing through two ion-exchange columns packed with Dowex 50W-X8 in Na^+ and H^+ forms respectively to desalt associated inorganic ions and neutral molecules. Finally an alkaline solution of fulvic acids at pH 7.5 was passed through a column packed with Dowex-1 X8 (80 to 120 mesh) in acetate form. A substantial amount of fulvic acids was adsorbed and the eluate obtained had light yellow colour. The fulvic acids were precipitated with barium hydroxide after acidifying with hydrochloric acid, dried at 40°C and were kept for analysis.

Chromatographic Separation

Paper chromatographic technique was used in the separation of the components of humic and fulvic acids. The technique included ascending, descending, circular and two-dimensional chromatographic methods using acidic, basic and neutral solvents. Among these the circular technique was found to be most suitable and versatile and hence used extensively. In the acidic solvents, systems such n-butanol-acetic acid-water, n-butanol-formic acid-water, n-propanol-formic acid-water and iso-propanol-formic acid-water, the varying proportions of individual components were examined in detail. As far as neutral solvent system is concerned many solvent mixtures of different compositions were tried, amongst which methyl-ethyl ketone—absolute alcohol-water, benzene-acetone-water, dioxane-acetone-water and acetone-methanol-water were examined in detail.

Only methyl-ethyl ketone-absolute alcohol-water (6:3:1 v/v) was found to some extent useful but the results obtained were not very satisfactory. Attention was then diverted toward basic solvent systems a few of which are specific for indolic and phenolic acids and related compounds. A few systems as given below were tried in detail. Three such systems investigated were (i) n-butanol-pyridine-water, (ii) n-butanol-pyridine-dioxane and (iii) iso-propanol-ammonia-water. The two most successful solvent systems in separating these acids on paper chromatograms were found to be: (i) iso-propanol: ammonium hydroxide (0.88 N): water (20:1:2 v/v) and (ii) n-propanol: formic acid: water (10:4:1 v/v).

These systems are highly sensitive for their composition, and slight change in it affects the results to a great extent. Pure humic acids sample in sodium form (Na^+) was obtained from a Swiss Firm—Chemische Fabrick—under the trade name 'FLUKA' for comparison and correct assessment (Table 2, Sl. No. 1).

For running the chromatogram, Whatman No. 1 filter paper was used in all the techniques, and the solvents used were of chromatographic grade except formic acid which was 98-100 per cent pure from E. Merck (Germany) and ammonium hydroxide of A.R. grade. The solution of the acids prepared and that procured were made in 0.5 N sodium hydroxide A.R. and a modest concentration of 1 mg/ml. was maintained. Strips were used in ascending and descending methods while circular papers of 26 cm. dia. were used for circular chromatography. All experiments were carried out at room temperature in the tanks saturated with vapours of the solvent.

Location Reagent

0.1 per cent (w/v) Bromo-cresol green was prepared in 99.5 per cent ethanol and made alkaline just before use to attain greenish blue colour at pH 7.2 in the case of basic solvent and at pH 7.8 in the case of acidic solvent. This solution was diluted five times to its volume with acetone. Both the spraying and dipping techniques were used to locate the spots. The chromatograms were fairly stable for many days when kept properly.

Carbohydrates and other sugars were found absent

in humic acids fraction and were detected in traces in fulvic acids when tested with anthrone[10]. The average organic matter was estimated with dichromate oxidation (Table 1). Other results are shown in Table 2.

TABLE 1—AMOUNT OF HUMIC MATERIALS RECOVERED FROM 500 g. OF SOIL

Fraction	*Organic Solvent Soluble, g.*	*Organic Solvent Insoluble, g.*	*Total Per Cent in Soil*
Humic Acids	0.0638	0.1215	0.037
Fulvic Acids	Nil	0.015	0.003

Discussions

Various methods have been used to extract organic acids of the soil but none seems to be acceptable without question. Nevertheless the use of mild alkali is preferred on account of its potentiality to extract the organic matter in maximum amount from soil. It is still open to question whether the substance so separated is the same as existed in the soil. In spite of this shortcoming, this method has been used and the sample obtained has been analysed by paper chromatography. If humic acids are accepted as a substance soluble in only alkali and insoluble in alcohol and other organic solvents, the fraction soluble in alcohol and other organic solvents in this preparation must correspond to hymatomelanic acids.[11] Hymatomelanic acids must again represent a group of acids consisting of not less than three components. The fact that increased solubility of alkali-soluble humic acids in methanol after washing with hydrochloric acid was noticed can be explained as a slow esterification of carboxyl -COOH and etherification of phenolic-OH groups. This supports the view that HA (O. S. S.) fraction is a result of mild oxidative hydrolytic reaction of HA (O. S. I.)[11]. If hymatomelanic acids fraction, viz. HA (O. S. S.), is excluded from being a part of true representative of humic acids, organic solvent-insoluble fraction of this preparation, i.e. HA (O. S. I.), should only form the true humic acids. This brownish-black fraction still shows five separate well-distinguished concentric rings on paper chromatogram with R_f values almost similar to that in the case of humic acids (Na^+) sample from Switzerland in solvent two and four such components in solvent-1 under the same experimental conditions (Table 2). This irregularity of varying number of components can be attributed to either different resolution

TABLE 2.—R_f VALUES OF HUMIC AND FULVIC ACIDS COMPONENTS

Sl. No.	*Fraction*	*Solvent 1*	*Time of Run, hr*	*Remarks*	*Solvent 2*	*Time of Run, hr*	*Remarks*	*U.V. Exam. Results in Solvents 1 & 2*
1.	HA(St) (Swiss)	0.705 0.615 0.384 0.125	6	Three golden yellow well spaced concentric rings with one component round centre	0.985 0.897 0.706 0.661 0.603	2½	Five concentric rings with no component left round the centre	Fluorescence of sky-blue colour at periphery before and after applying the L.R. R_f=0.984
2.	HA (O.S.I.)	0.683 0.609 0.380 0.108	6	as above	0.934 0.890 0.724 0.671 0.618	2½	as above	as above
3.	HA (O.S.S.)	0.739 0.666 0.131	6	Two golden yellow well spaced rings with one component at the centre.	0.975 0.615 0.537	2½	Three yellow rings with no component left at the centre	Two fluorescent rings that of higher R_f at periphery is brighter. R_f, 0.975, 0.658
4.	Fulvic acids FA	0.787 0.725 0.185	6	Same as above	0.975 0.902 0.634 0.585	2½	Four concentric rings of which that of lowest R_f is brightest and stable for more than a week.	Fluorescence of sky-blue colour at the periphery. Much stronger and wider band than in Nos. 1, 2 & 3. R_f=0.978

capability of the two solvents or due to their chemical effects during separation e.g. some easily oxidisable di-hydroxy phenolic compounds may be lost in the first solvent[12] but however the possibility of the former seems to be more reasonable in this case. In case of solvent-1 one component of the samples in each case is left round the centre (Table 2, with lowest R_f.) whereas this is not noticed with solvent-2. Which shows that the component left at the centre has also been moved and resolved by solvent-2. As regards the fulvic acids a similar result with four concentric rings are noticed. This is in agreement with Miklaszeswski's[13] results on fulvic acids. A close proximity that is noted here between hymatomelanic acids or HA (O. S. S.), HA (O. S. I.) and fulvic acids is the central component left on the chromatogram in solvent-1 and one fluorescent band of same (or nearly same) R_f values in each case in both the solvents.

The u.v. examination indicated the presence of one fluorescent substance in each sample, except HA (O.S.S.) which showed two such components (Table 2). These fluorescent bands are sensitive to sulphanilic acid-sodium nitrite reaction which indicates the presence of aromatic hydroxy and amino compounds. The sensitivity is stronger with fluorescent band of lower R_f in HA (O.S.S.). A two-dimensional chromatogram run in solvent-1 followed by solvent-2 using ascending technique showed that the size and intensity of u.v. fluorescence in HA (O.S.S.) and fulvic acids are similar and stronger than those in the case of HA (O.S.I.) and Swiss sample.

It is concluded that in all, HA (O.S.S.) represents three and HA (O.S.I.) five components and at least four acid components exist in fulvic acids. Moreover, considering the methods of extraction purification, paper chromatographic separation and their solubilities in hydrochloric acid and sodium hydroxide, it is assumed that fulvic acids are ampholytic in nature i.e. they contain basic and acidic salt-forming groups in the molecule, whereas humic and hymatomelanic acids molecules contain only acidic groups capable of formic alkali salts. The presence of this basic group in the molecule of fulvic acids may be held responsible for all its differences from humic acids and hymatomelanic acids.

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Use of Air from Nitric Acid Turbo-Compressor for Deriming Cold Boxes in Air-Liquefaction Units of an Ammonia Plant

By

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An alternate source of air for deriming the air fractionation cold boxes at the Nangal fertilizer plant has been proposed, which will spare the compressor for the planned annual maintenance thus saving at least 2 days' production. The deriming air requirements of about 1200Nm³/hr can be drawn from either of the two 55,000Nm³/hr capacity turbo-compressors of the nitric acid plant. In this paper the feasibility of the above proposal has been examined in the light of the following considerations: (1) whether the existing system of decarbonation would scrub out adequately the carbon dioxide in the deriming air. A plot of K_Ga against pressure has been prepared for the prevalent liquid rate of 19.700 kg/hr.m² in the caustic soda scrubbers and for an operating temperature of 25°C; the calculations for the revised system based on above noted plot have been worked out; (2) the calculations for pressure drop and on the flooding conditions in the towers have been used as a guide to find out whether the proposed operating conditions would give a reasonable tower performance; (3) the suitable operating conditions have been specified in the light of (1) and (2); and (4) the modifications in the deriming line have been proposed to accommodate the higher actual flow rate. The actual deriming carried out based on the revised proposal has been found to work very satisfactorily.

The study relates to utilization of air from the turbo-compressors of the Nitric Acid plant for deriming of cold boxes of the Air Liquefaction units in Ammonia plant. The cold boxes after working continuously for some time—about a year—get some deposits of oil, moisture, carbon dioxide, etc., leading to lower efficiency and operating troubles. It has then to be derimed with warm and decarbonated dry air. It takes nearly 6 days to derime a unit and put it back into operation. The designers envisaged the use of air from the main air compressor for deriming. Looking to the requirement of the downtime for the annual maintenance and overhauling of the air compressors, a portable air compressor was being contemplated as an alternative source of air supply, otherwise in a year 6 days for deriming and another 7 days for compressor maintenance will be the downtime for the unit. A portable air compressor was once tried but due to low capacity its operation was not very successful. A higher capacity compressor was, therefore, considered. Meanwhile a suggestion came from the Mechanical Maintenance section for utilizing air from turbo-compressor, available at 220°C and 3.5 ata. A study was, therefore, conducted to verify the capability of the decarbonation towers to scrub carbon dioxide from the turbo-compressor air.

It has become feasible as a result of this study to use air from the turbo-compressors for deriming the cold box after decarbonating it in the present system, provided (i) its temperature is brought down to about 27°C; and (ii) the existing deriming air line after the desiccator is modified, and its size increased so as to deliver sufficient air.

The performance of the system for deriming operations carried out on Air Liquefaction unit No. 1 during the last week of March 1964 has come up well according to expectations. The deriming was completed in 100 hr. The pressure being low (2.5 ata), the moisture (as water vapour) carried by the air was comparatively high, causing choking in the drain line of the desiccator. However, the difficulty was overcome by keeping the drain valve somewhat open and drain the water more frequently.

The existing air liquefaction system and the proposed deriming system have been described briefly here with flow diagrams for explaining the existing and the proposed systems. The scope of this study covers the

following: (a) whether the existing decarbonation system would scrub out adequately carbon dioxide from the alternate source of air under the changed operating conditions; (b) the towers would operate satisfactorily with respect to the column loading and pressure drop across them; (c) specifying the operating conditions would ensure a fair degree of success of the proposed system.

Air Liquefaction Section (Fig. 1)

It consists of two identical air fractionation units, each having an independent 1,500 cv (h.p.) motor driven, horizontal three stage, six cylinder air compressor, capable of delivering 6,000 Nm³/hr. of air at 13 kg/cm² under normal operating conditions and at 20 kg/cm² maximum during the cooling down period on start-up.

The air from the fractionation unit is delivered to the decarbonation section comprising two towers in series, each packed with 3 m³ of 1 in. × 1 in. steel Raschig rings. Each tower is provided with a pump for circulating 8-10 per cent caustic soda solution at 16 m³/hr. A separator is provided downstream of the towers to separate entrained caustic soda, and decarbonated air is led into the cold box.

The air enters one of the warm exchangers—the other being a standby kept ready for changeover—and cools down to −70°C, and thus gets freeze-dried depositing its moisture and traces of carbon dioxide. The dried air passes to a liquefier exchanger from which about 90 per cent of the air is withdrawn after it cools down to −140°C and expanded through an expansion engine to the medium pressure column (Fig. 1). The remaining 10 per cent get liquefied at the bottom of the liquefier, from where it is also sent to the medium pressure column, operating at 4.5-4.8 kg/cm², through an expansion valve. A rich liquor with 40 per cent oxygen is delivered from the bottom of the M.P. column through an acetylene adsorber and then a cooler as feed into the low pressure column, operating at 0.4 kg/cm² pressure. Liquid nitrogen reflux to the L.P. column is supplied via a subcooler from a tray located below the vaporiser-condenser in the M.P. column.

Pure gaseous nitrogen is withdrawn from the top of the L.P. column and 95 per cent gaseous oxygen from its bottom. These products are led back through the

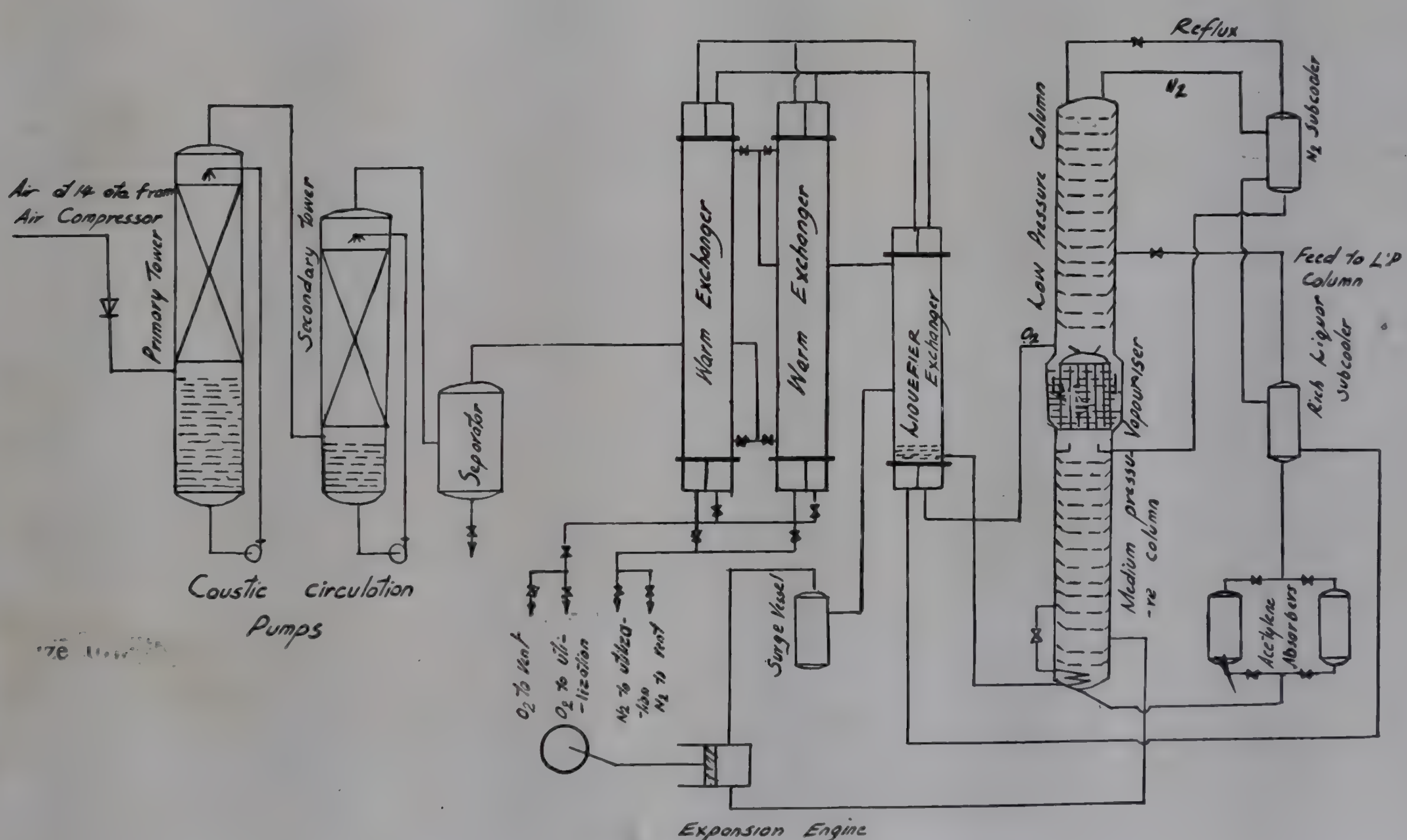

Fig. 1—Air Fractionation Unit Treating 6000 Nm³/hr Air

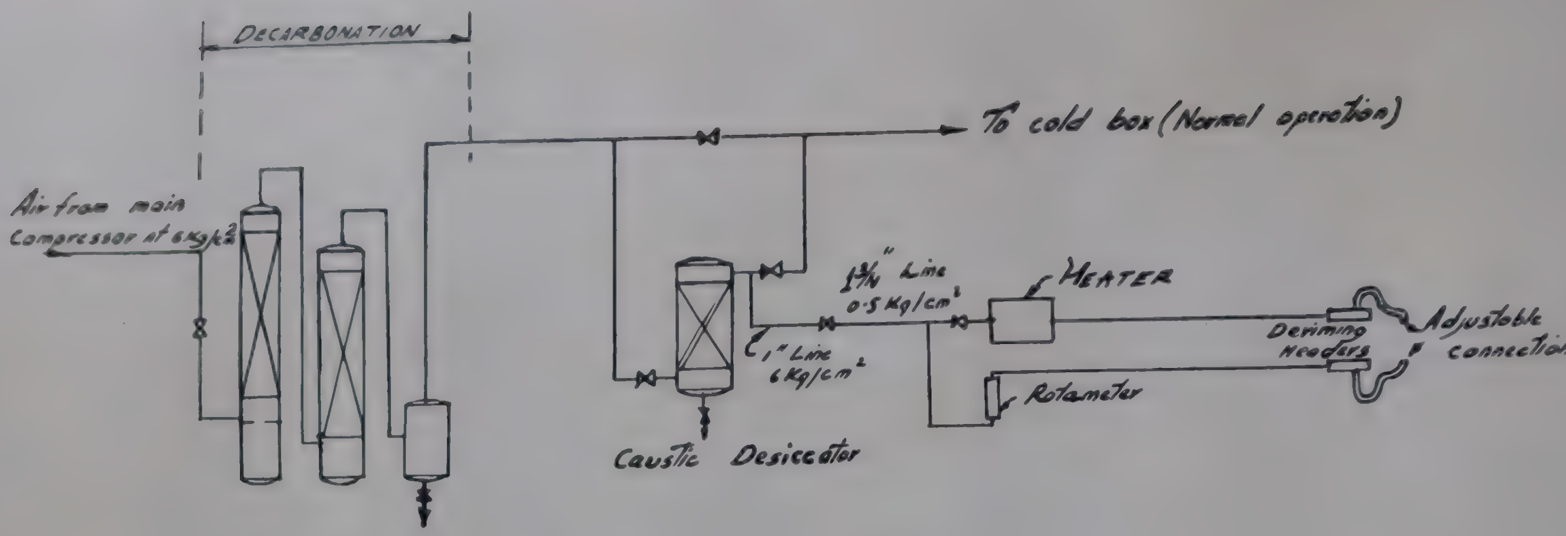

Fig. 2—Existing System of Deriming

exchangers to cool the incoming air. Each unit thus produces about 4,700 Nm^3/hr. of nitrogen containing an oxygen impurity of less than 7 ppm and about 1,300 Nm^3/hr. of oxygen of 95 per cent purity.

The existing system of complete deriming of the cold boxes is as follows: Air from the compressor, operated at about 6 kg/cm^2 final discharge pressure, is decarbonated and led for moisture removal through a desiccator containing 2 in. lumps of caustic soda (Fig. 2). It is then delivered through a valve into the deriming system at 0.5 kg/cm^2. Adjustable connections are provided to deliver the deriming air to any particular circuit by suitably connecting them up.

Proposed System of Deriming

The proposed system envisages the use of turbo-compressor air available at 3.5 ata and 220°C at the nitric acid end of the Nitric Acid plant. This air is to be cooled and delivered at the inlet of the decarbonation system. The air compressor can thus be made available for the scheduled overhaul and maintenance simultaneously with the scheduled deriming of the cold boxes (Fig. 3).

Feasibility of the Proposed System

(*a*) *Absorption of CO_2 in NaOH Solution:* Tepe and Dodge[1] have measured the rate of carbon dioxide

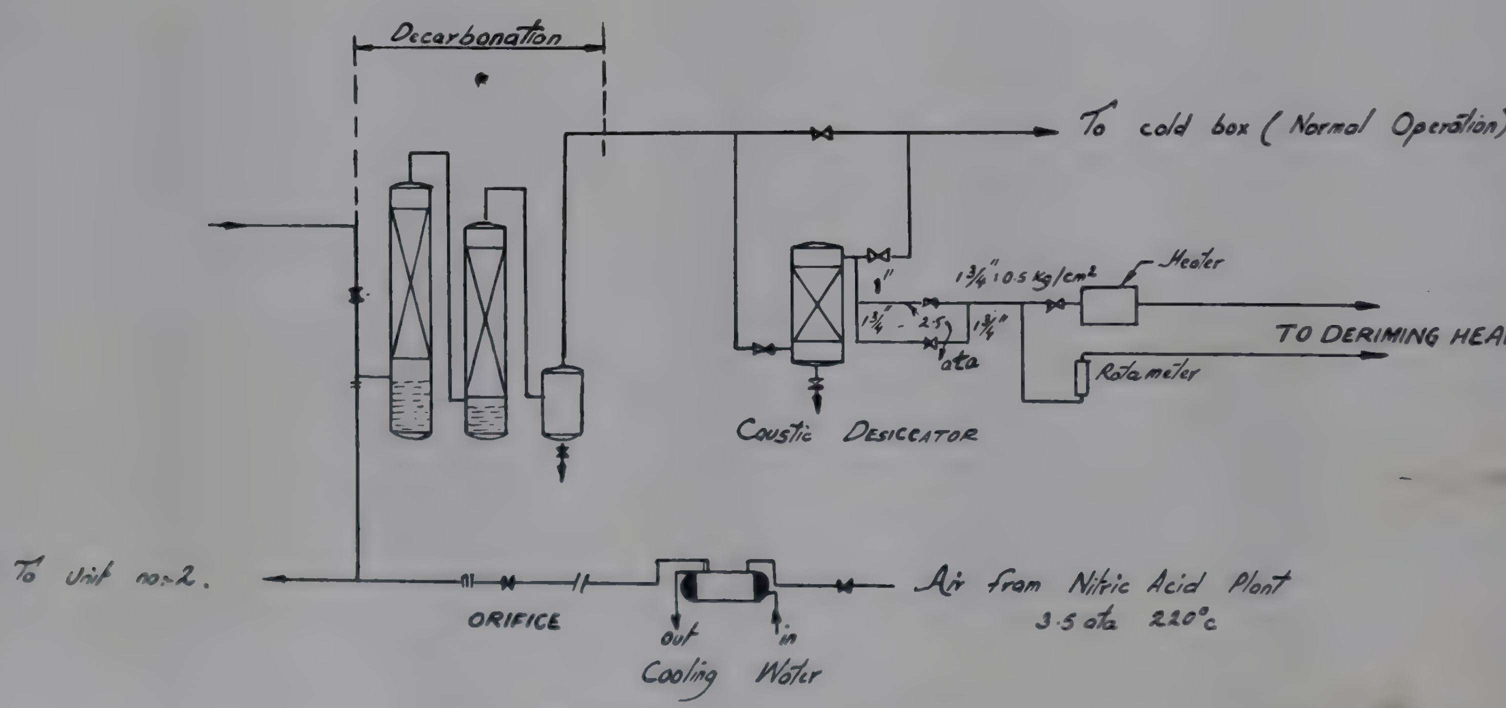

Fig. 3—Proposed System of Deriming

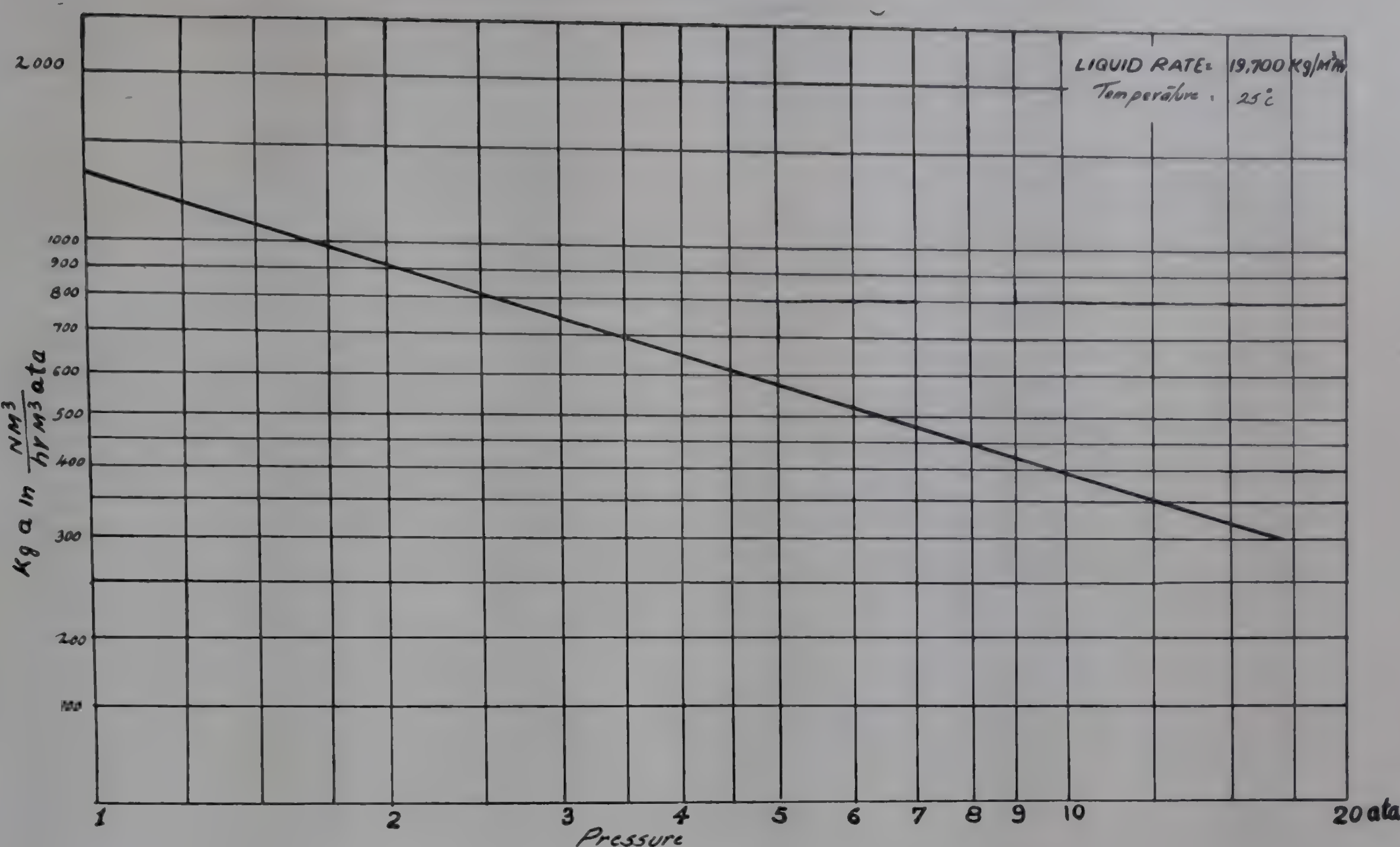

Fig. 4—Nomograph

absorption from air with circulating caustic soda solution. Their findings are that the absorption coefficient (i) increases rapidly with increasing concentration; (ii) is independent of the gas flow rate and increases with 0.28 power of the liquid rate within the range of 800 to 10,000 lb/hr/sq. ft.; and (iii) increases with the sixth power of the absolute liquor temperature between 78° and 123°F (22.5° to 50.5°C). Spector and Dodge[1] experimented up to 100 psi pressure and found that the absorption coefficient (a) varied from 0.15 to 0.35 power (of gas rate lb/hr/sq. ft.), but attributed this to lower range of carbon dioxide gas concentration; (b) decreased with 0.5 power of the absolute tower pressure; (c) was 20 to 30 per cent higher with caustic potash than with caustic soda; and (d) a commercial-size tower appeared to give results about 9.5 to 12 per cent higher than the experimental ones.

In keeping with the above and from the data of Tepe and Dodge[1] a nomograph has been prepared corresponding to the liquid rate of 19,700 kg/cm.² hr. in decarbonation towers (Fig. 4).

The basic equation considered for designing a decarbonation tower is:

$$K_G a = \frac{N}{V. \triangle P_{LM}} \qquad (1)$$

where,

$K_G a$ =the coefficient of total absorption $Nm^3/hr.m^3$ ata.

a =the active and wetted unit surface of the packing in the tower in M^2/M^3.

N =rate of CO_2 absorption Nm^3/hr.

V =volume of the packing m^3

$$P_{LM} = \frac{P_G - P_{G_2}}{L_n \frac{P_{G_1}}{P_{G_2}}} = \frac{P_{G_1} - P_{G_2}}{2.3 \log \frac{P_{G_1}}{P_{G_2}}} \text{ in which}$$

P_{G_1} =the partial pressure of CO_2 in gs entering gas in ata.

P_{G_2} =the partial pressure of CO_2 in outgoing gas in ata, and

Calculations

The new conditions of operation for decarbonation were assumed as below, and the calculations are based on them:

(*a*) Quantity of air to be handled =1200Nm³/hr.
Air inlet pressure at decarbonation =2.5 ata.
Air inlet temp. at decarbonation =27°C

(*b*) No, of towers =2 in series
Tower dia. =1.07 m
Tower cross section $=0.9\ m^2$
Packing volume per tower $=3\ m^3$
Packing =1 in.×1 in.×0.8 in. steel Raschig rings

Caustic liquor circulation rate in each tower $=16\ m^3/hr.$
Caustic strength =10% (1.108 g/ce density)

(*c*) *Present Tower Performance under Normal Operating Conditions*

Quantity of air to be handled $=6000\ Nm^3/hr.$
Tower cross section $=0.9\ m^2$
Gas rate $=8650\ kg/hr.m^2$
Liquid rate $=19{,}700\ kg/hr.m^2$ (say 20,000 $kg/hr.m^2$)
Working pressure =14 ata.
Total packing volume $=3\times2=6m^3$
From Nomograph (Fig. 4.) K_Ga $=340\ Nm^3/hr.m^3$ ata.

Based on the above value of K_Ga, carbon dioxide content in the exit air after decarbonation is as below:

CO_2 in the inlet air =0.03%(300 ppm)
Total CO_2 in the air $=1.8\ Nm^3/hr.$

Now from equation (1)

$$\triangle P_{LM}=\frac{N}{V\times K_Ga}=87.25\times10^{-5}\text{ ata.}$$

$$\triangle P_{LM}=\frac{P_{G1}-P_{G2}}{L_n\frac{P_{G1}}{P_{G2}}}\approx\frac{P_{G1}}{L_n\frac{P_{G1}}{P_{G2}}}$$

$$P_{G_1}=\frac{0.03\times14}{100}=420\times10^{-5}\text{ ata.}$$

$$Ln\frac{P_{G_1}}{P_{G_2}}=\frac{P_{G1}}{\triangle P_{LM}}=4.87$$

$$\frac{P_{G1}}{P_{G2}}=130$$

$$P_{G_2}=\frac{P_{G_1}}{130}=2.3\text{ ppm.}$$

Actual conditions of the system show carbon dioxide content in air exit decarbonation to vary between 0.9 and 2 ppm. The calculated results are quite close to the actual ones, rather somewhat on the conservative side.

(*d*) *Tower Performance under the Proposed Conditions*

(i) *CO_2 Removal:* The actual performance of the tower having been checked and the method of calculation ascertained to represent adequately the working of the system under normal operating conditions, the volume of the packing required for the proposed scrubbing of 1200 $Nm^3/hr.$ of air at 2.5 ata and 25°C has been worked out, the liquid rate and caustic concentration remaining unaltered.

$$CO_2\text{ to be absorbed}=12\times\frac{0.03}{100}=0.36\ Nm^3/hr.$$

$$P_{G_1}=\frac{0.03\times2.5}{100}=75\times10^{-5}\text{ ata.}$$

Assuming 1 ppm. CO_2 in the exit scrubbers:

$$P_{G_2}=\frac{0.0001\times2.5}{100}=0.25\times10^{-5}$$

$$\triangle P_{LM}=\frac{P_{G_1}-P_{G_2}}{Ln\frac{P_{G_1}}{P_{G_2}}}=13.1\times10^{-5}$$

K_Ga (Fig. 4.) $=825\ Nm^3/hr.\ m^3$ ata.

Applying a safe factor (0.5) to the value of K_Ga ($825\times0.5=413$, say 420), the packing volume required by substituting proper values in equation (1) 420 $=\frac{0.36}{V\times13.1\times10^{-5}}$ from where $V=6.55\ m^3$.

Now assuming carbon dioxide in the outlet air from decarbonation as 2 ppm, the value of $P_{LM}=\frac{74.5\times10^{-5}}{Ln\frac{300}{2}}$ $=14.85\times10^{-5}$ ata.

$K_Ga=420$

$$\text{Then packing volume}=\frac{0.36}{420\times14.85\times10^{-5}}=5.77\ m^3.$$

The actual volume of the packing is 6 M^3. It is, therefore, concluded that under the proposed conditions, carbon dioxide content in the exit air varies between 1 to 2 ppm, when K_Ga is assumed as 50 per cent of the value determined from the nomograph (Fig. 4).

(ii) *Estimate of Flooding Conditions:*

Liquid rate (GLF) $=19{,}700\ kg/hr.\ m^2$

$$=\frac{19.700\times2.2}{10.76}\text{ lbs/hr.sq.ft.}$$

=4030 lb/hr.sq.ft.

Let G_{CF} represent gas rate at flooding.

Factor $\frac{aV}{F^3}$ for Raschig rings[2] $(25 \times 25) = 185$

Liquid viscosity (μ_1) $=$ I (C.P.)

Gas density (Pg) at

2.5 ata. $= 0.0808 \times \frac{273}{300} \times \frac{2.5}{1}$

$= 0.183$ lbs/cft.

Liquid density (P_1) $= 62.4 \times 1.108 = 69$ lbs/cft.

g $= 32.2$ ft/sec.^{2}

From the graph[2]

Ordinate (γ) $$= \left(\frac{G_{LF}}{3600}\right)^2 \times \frac{a_V}{F^3} \times \frac{\mu_1^{0.2}}{(P_L)^2 g}$$

$$= \left(\frac{4030}{3600}\right)^2 \times 185 \times \frac{1}{(69)^2 \times 32.2}$$

$= 0.001517$

From the graph (Fig. 4)

abscissa (X) $= 0.10$

$$\frac{G_{LF}}{G_{CF}}\left(\frac{P_G}{P_L}\right)^{0.5} = 0.10$$

$$G_{CF} = \frac{4030}{0.10}\left(\frac{0.183}{69}\right)^{0.5}$$

$= 2040$ lbs/hr. sq. ft.

Proposed operating gas rate $$= \frac{1200 \times 29}{22.4 \times 0.9} \times 1730 \text{ kg/hr. m}^2$$

$= 354$ lbs/hr.sq.ft.

The operating gas rate would be far below the tower flooding conditions.

(iii) *Linear gas velocity (empty cross section basis):*

Linear velocity under proposed condition $$= \frac{1210 \times 300 \times 1}{273 \times 2.5 \times 3600 \times 0.9}$$

$= 0.16$ m/sec.

The linear velocity under the proposed conditions is comparable to the normal operating conditions.

(iv) *Pressure Drop Across the Tower:*

Linear Gas Velocity $= 0.16$ m/sec.

Liquid rate $= 16\ m^3$

$$\frac{16}{0.9} = 17.8 \text{ m}^3\text{/hr. m}^2$$

Gas specific weight under proposed operating conditions $$= 1.2928 \times \frac{273}{300} \times 2.5$$

$= 2.94$ kg/m^3

Liquid viscosity $= 1°$E

Total packed height for both towers $= 2 \times 3.6$ m $= 7.2$ m

Pressure drop from Krisebhaum nomograph $= 5$ mm H_2O/m. of packing.

Total pressure drop in decarbonation towers $= 5 \times 7.2 = 36$ mm. H_2O.

(v) The existing deriming system supplies air from the high pressure side at 6 kg/cm^2 into the deriming circuit at 0.5-0.6 kg/cm^2 through a globe valve. The line size is 1 in. before (H.P. side) and $1\frac{3}{4}$ in. after the valve (L.P. side). Since the H.P. side of the system under proposed conditions would now be at 2.5 ata (assuming negligible pressure drop across the towers and related piping), actual air flow through the 1 in. line would correspondingly increase in the ratio of 7: 2.5 or 2.8 times as much. The line size that would deliver this amount of air at the earlier flow rate

$= \sqrt{2.8}$ times the original dia. of the pipe.

$= \sqrt{2.8} \times 1$ in. $= 1.67$ in. say $1\frac{3}{4}$ in.

(vi) The decarbonation is reported to improve quite rapidly with the increase in the caustic liquor temperature in the process between 25.5° and 50.5°C. However, since the moisture content would increase with the increase in temperature thereby increasing the load on the desiccator, it would be advantageous to keep 27°C as the operating temperature.

(*e*) From the foregoing calculations, it clear that the proposed system would serve the purpose with a fair degree of success. As a result, the following conditions can be specified: (i) Minimum air pressure available at decarbonation inlet at the primary tower should be 2.5 ata; (ii) temperature of the air inlet at the primary decarbonation tower should be 25° to 27°C; (iii) Adequate quantity of air up to 1200 Nm^3/hr. should be available at the decarbonation inlet; (iv) the high pressure side line of the deriming air system should be replaced by a $1\frac{3}{4}$ in. size line—the same size as the low pressure side line.

Actual Performance of the System

The piping and gas coolers at nitric acid end and the necessary valves were designed and erected in March 1964. On March 28 1964, the Air Liquefaction Unit No. 1 was shut down at 7.30 a.m., when the necessary modification was carried out on the primary tower inlet line and the new system was fitted up. An orifice plate was installed to indicate the flow of air. The deriming air line was supplemented by an additional line of the same size as of the existing one after the pressure control

valve, as envisaged earlier. All these jobs were over by 12 noon and deriming was started.

The derming of the complete cold box was over on April 1, 1964, i.e. after 100 hr. All the cold box outlet points were warmed up to about 25°C. The initial air-flow was about 400 Nm³/hr., which was brought up later to about 1100 Nm³/hr. as deriming progressed. The average air-flow during the deriming period was 560 Nm³/hr.

The temperature of the air available at the decarbonation during the period remained about 33°C. This is higher than the stipulated temperature, viz. 27°C. Some evidence of increased load on the desiccator was noticed as its drain choked often and the draining became relatively difficult. The pressure remained about 2 kg/cm^2 throughout the period of deriming and the minimum observed was 1.8 kg/cm^2 at the decarbonation outlet, when the flow-rate was 1120 Nm³/hr.

With the supplementary deriming air line, all the required amount of air up to about 1100 Nm³/hr. could be delivered without any difficulty.

The performance of decarbonation of air was quite satisfactory After handling all the air required for deriming, the secondary decarbonation tower did not have had any noticeable change in caustic soda concentration in the circulating caustic liquor, evidently the primary decarbonation tower was more than adequate to remove all the carbon dioxide, its amount in the decarbonated air exit secondary tower being only 1 to 2 ppm.

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Bulk Blending and Compatibility of Fertilizers*

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Numerous ratios of nutrients are needed to meet adequately the agronomical requirement of a large country like India. Bulk blending under such conditions provides an essential supplement to the production of complex and chemically mixed fertilizer, the nutrient ratio of which is obviously limited to some of the more important formulations. Some of the important problems arising as a result of bulk blending have been discussed here.

In India the average yield per acre of agricultural produce is extremely low. Balanced fertilization is, therefore, essential. The primary nutrients are nitrogen, phosphorous and potassium, and deficiency of soil with respect to any one of these affects seriously the yield. Repeated use of any one of the nutrients alone is harmful for the soil. It has been found that during the first phase of development of agriculture, phosphates are as important as nitrogen. The need of potassic fertilizers is felt later.

World's consumption of fertilizers at present, indicate that nitrogeneous, phosphatic and potassic fertilizers are consumed in comparable amounts. In India the total consumption of fertilizers for the year 1960-61 was 283,100 metric tons of N, 58,000 metric tons of P_2O_5 and 28,900 metric tons of K_2O. Low consumption

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of K_2O is understandable but the consumption of P_2O_5 is extremely low. There has been some improvement during 1961-62 with regard to the consumption of phosphatic fertilizers, but it is not sufficient to meet the deficiency. Moreover, useful reserves of phosphorus is essential to maintain the fertility of soil.

Union Ministry of Food and Agriculture in collaboration with the U.S. Technical Cooperation Mission made a study of India's agronomical requirement, and came to the conclusion that six nutrient ratios would meet our immediate requirement. The ratios are: 1 -1-0; 1-2-0, 2-1-0, 1-1-1, 1-2-1 and 2-1-1. Dr. Raymond Ewell, U.S. delegate to the ECAFE conference, held in November-December 1963 at Bombay, proposed for India the following nutrient ratios, viz. 1-1-0, 2-1-0 and 1-2-0, where potash is not needed, thus confirming the recommendations of the Union Ministry of Food and Agriculture and the U.S. Technical Cooperation Mission.

The advantages in the application of multinutrient mixture over straight applications are fair distribution of plant nutrient, saving of time, reduced cost of storage and transportation. It is estimated that in 1962 about 22 per cent of the total fertilizer consumed in this country were in the form of mixtures. The corresponding figures for the U.K. and U.S.A. are about 60 and 70 per cent respectively. About 40 per cent of the mixed fertilizers used at the moment in U.S.A. are bulk-blended mixtures.

The biggest problem in the production of mixed fertilizers whether in the form of chemically mixed granules or simply blended in dry form is to maintain the desirable keeping quality. Some of the nutrients when mixed together become highly hygroscopic and the product has a strong tendency to cake. In some cases, the product becomes moist and too plastic, whereas in a few cases mixing leads to a significant loss of nutrient. These factors are very well represented† in Fig. 1. As is indicated, the compatibility of various constituents is not much of a problem, when the mixture is prepared at site and distributed immediately.

Mixed fertilizers having desirable storage property is more essential for India and possibly to other countries of the south-east Asia, where the ambient conditions and temperature are generally high and due to lack of adequate distribution facilities for quick disposal of the fertilizer, considerable time elapses between the mixing and application to the soil.

† Adopted from 'Fertilizer Use' by A. Jacob and H. V. Uexküll, (Verlaggesellschaft fur Ackerham mbH, Hannover) 1960, ·73.

Most of the mixed fertilizer produced in India at present are as a result of dry blending of primary nutrients. The mixing is carried out in small batches without giving due consideration to the keeping quality or the uniformity of the product so produced, with the result that cultivators often receive the mixed fertilizer in a caked condition. They have to break the lump before its application to the fields.

This is regrettable especially when the utility of mixed fertilizers is not fully appreciated by the consumers, and a bad product will undoubtedly create unfavourable impression regarding its use among the users.

It may be worthwhile, therefore, to discuss the compatibility of fertilizers when blended in dry form. Because from cost considerations and greater flexibility, the blending of solid nutrients is, and likely to remain, in future popular with producers, distributors and consumers alike.

Hygroscopicity

A fertilizer absorbs moisture when the relative humidity of surrounding air is higher than its critical relative humidity i.e. ratio of vapour-pressure of saturated solution to the vapour pressure of saturated air at that temperature. The critical relative humidity of some of the fertilizers is given below (Table 1).

TABLE 1—Critical Relative Humidity at 30°C

Fertilizer	*Critical Relative Humidity, %*
Ammonium Nitrate	59.4
Ammonium Sulphate-Nitrate	62.3
Urea	72.5
Ammonium Chloride	77.2
Ammonium Sulphate	79.2
Diamonium Phosphate	83.0 (at 26.7°C)
Monoammonium Phosphate	91.6
Monocalcium Phosphate*	93.7
Potassium Chloride	84.0
Potassium Nitrate	90.5
Potassium Sulphate	96.3

* Water soluble constituents of superphosphate.

Although calcium ammonium nitrate contains 40 per cent by weight of inert and non-hygroscopic material like limestone, it is slightly more hygroscopic than ammonium nitrate. Employment of more than one nitrogenous fertilizer as nitrogen-carrier in the preparation of a mixed fertilizer should be done with care. With the exception of ammonium sulphate,

other nitrogenous fertilizers when mixed together give a product which is more hygroscopic than their constituents. Ammonium sulphate is favourite with bulk blenders as it is relatively less hygroscopic and compatible with phosphatic and potassic fertilizers. Monocalcium phosphate, the main soluble constituents of superphosphate or triple phosphate, is non-hygroscopic. But when it is mixed with ammonium nitrate (or CAN), the resulting product is as hygroscopic as ammonium nitrate.

Ammonium phosphates are relatively non-hygroscopic and can be mixed, if necessary, with other fertilizers to give high analysis mixtures.

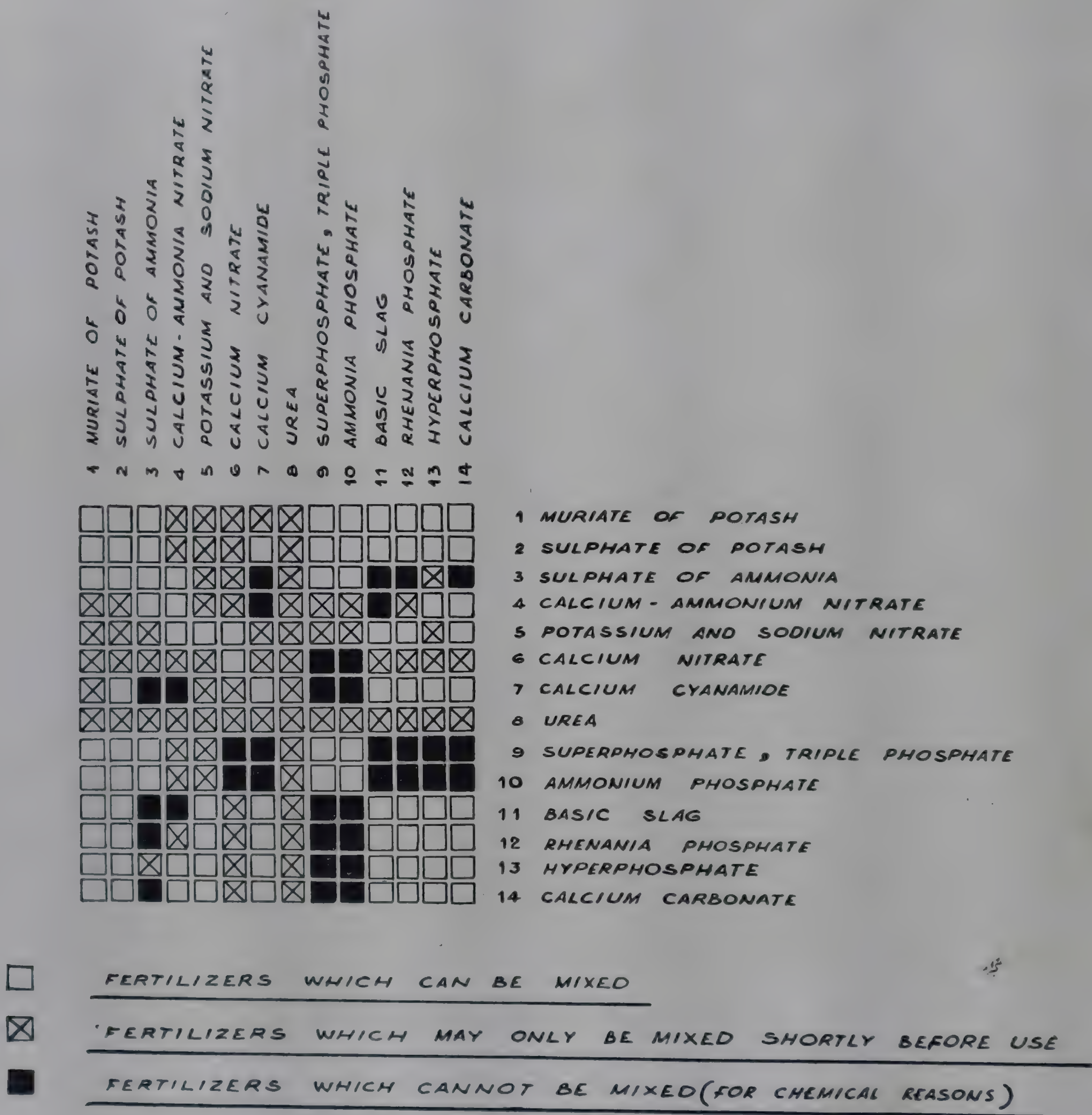

Fig. 1—Guide for Mixing Fertilizers

Caking

Caking is normally caused by recrystallization of the soluble material between the particles of fertilizer; the extent of caking increases, depending upon the temperature coefficient of solubility of the fertilizer, by repeated crystallization and dissolution of the fertilizer on account of fluctuation in the ambient temperature. The cake hardens on account of pressure, invariably present, during storage. Sometimes the cakes are so hard that considerable time and labour are required to make the fertilizer suitable for application in the fields.

It is clear from the above that moisture is the main cause for caking. In the case of mixed fertilizers, the moisture may be present initially in any of their constituents or it may be absorbed later. The latter can be checked by bagging the fertilizer in a moisture-proof bag. But it is difficult to control the former as apparently dry superphosphate normally contains 6-10 per cent of moisture and this is sufficient to dissolve considerable quantity of nitrogenous fertilizer.

Another factor which also contributes to caking in mixed fertilizer is the occurrence of chemical reactions. Some of the more important reaction occuring in presence of moisture are:

$$Ca(H_2PO_4)_2+(NH_4)_2SO_4 = CaSO_4 + 2NH_4H_2PO_4$$
$$NH_4NO_3 + KCl = NH_4Cl + KNO_3$$
$$(NH_4)_2SO_4 + 2KCl = 2NH_4Cl + K_2SO_4$$

In the case of a chemically mixed fertilizer, these reactions do not present much of a problem, because the product obtained after granulation and drying is more or less cured. In dry blending, however, these become important if the product contains sufficient moisture. Thus, caking can be minimized only if the constituents are dry.

Moistness

There appears to be some confusion between moistness and hygroscopicity of the mixed fertilizer.

Moistness may not necessarily arise because of hygroscopicity of the product. For example, the experience of the state cooperatives who blend the straight fertilizers is that urea and superphosphate when mixed together become highly hygroscopic and moist if the proportion of urea is higher than 8-10 per cent.

Moistness in this case may be arising on account of transfer of moisture from non-hygroscopic superphosphate to urea which is more hygroscopic. As stated earlier, superphosphate contains up to 10 per cent moisture. Urea takes up miosture, and because of high solubility of urea in water, the bulk of liquid phase in the mixture increases to about twice the volume of water and the product becomes moist and loses free-flowing characteristics. Similar situation arises in the case of ammonium nitrate or calcium ammonium nitrate. In the case of calcium ammonium nitrate its granular form may be completely destroyed.

Loss of Nutrient

Experiments carried out at Sindri show that there is marked reversion of water-soluble P_2O_5 into citrate-soluble and to a lesser extent, reversion of citrate-soluble into citrate-insoluble if superphosphate is mixed with calcium ammonium nitrate and allowed to stay together. Reversion is found to be less if the moisture is low and the particles of the ingradient coarse. Further investigations carried out indicate that reversion can be minimized by using dolomite as a diluent for ammonium nitrate instead of highly calcareous limestone presently being used. Part of the reversion of water-soluble into citrate-soluble is on account of reaction between monocalcium phosphate and limestone present in calcium ammonium nitrate as shown in the following equation:

$$Ca(H_2PO_4)_2+CaCO_3=2\ CaHPO_4+CO_2+H_2O$$

Therefore, blending of superphosphate and calcium ammonium nitrate should be avoided.

It has been experienced that there is sometimes a strong smell of ammonia in the atmosphere particularly in summer when urea is blended with superphosphate. Lundstrom and Whittker[1] observed some decomposition of urea in presence of monocalcium phosphate. Decomposition of urea was significant even at a temperature of 45°C. There is also a possibility that free phosphoric acid present in superphosphate may have an accelerating effect on hydrolysis of urea.

$$CO(NH_2)_2+H_2O=2NH_3+CO_2$$

Segregation

Non-uniformity is a serious problem in many dry blended granular fertilizer with the result that desired distribution of nutrients in the soil is affected. Granular size has been found to be the dominant factor in the segregation of ingradients of a mixture. The shifting of small granules through the void spaces between

larger granules having different nutrient content, together with rolling action of larger granules contribute to segregation. Uniform particles size of ingradients alleviate segregation.

Formulation

A 8-8-8-fertilizer is guaranteed to contain 8 per cent N, 8 per cent of available P_2O_5 and 8 per cent of water soluble K_2O. If the constituents are superphosphate (18% available P_2O_5), ammonium sulphate (21% N) and potassium chloride (60% water soluble K_2O), the fertilizer of above grade would require 160 lbs of N, 160 lbs of available P_2O_3 and 160 lbs of water soluble K_2O per 2,000 pounds of blended fertilizer. Therefore,

$$\text{Ammonium sulphate needed} = \frac{160}{0.21} = 762 \text{ lbs. (approx.)}$$

$$\text{Superphosphate needed} = \frac{160}{0.18} = 889 \text{ lbs. (approx.)}$$

$$\text{Potassium chloride needed} = \frac{160}{0.60} = 267 \text{ lbs. (approx.)}$$

Total	1918/2000 lbs.
Free pound space available	82 lbs.

Some free pound space is necessary to make an allowance for the moisture content of the ingradients. If superphosphate contains seven per cent moisture in the above formulation, then about 62 lbs cent of the free pound space available will thus be utilized. More free pound space will be required of bone meal, pesticides or conditioning agents are to be added.

Varying ratios can be obtained with the above ingradients. By using ammonium phosphate as a P_2O_5 source material, high analysis mixtures can be obtained.

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Reprography*

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Documentation or communication of scientific and technical information depends mostly on reprographic measures. Various processes adopted to obtain fascimile or micro copies and enlargements, basic principles on which they work and newer developments which result in economy and time-saving have been indicated in this article.

Documentation and information work involve a variety of functions. They constitute mainly of collection, registration and classification of documents—the extraction and processing of information contained in documents in a language in which the reader is conversant—and finally the storage, retrieval and supply to the interested users. Each of these functions has its own complexity and entails some problems which a documentalist has to overcome to attain scientific documentation. The last-named function, viz. the supply of the recorded knowledge to the users, is not a simple one. The document can be lost in the transit due to some unforseen event. Also, the different users cannot be served readily by a single document especially if they be at different places, and the very purpose of prompt dissemination of information will be defeated if a single document is to be routed through the interested users in succession. Besides, the old and dilapidated documents cannot be left at the mercy of time, and therefore require to be renovated. Therefore, a technique has to be developed for an important function of documentation, viz. the communication of information. This technique, called Reprography, is

* Based on a series of lectures delivered at the regional documentation training course held at INSDOC (CSIR) New Delhi during October-November 1963, which was attended by author.

concerned with both reproduction and photography.

Now-a-days, reprography is meant to be used in a wider sense. It means reproduction by any method of articles, figures, drawings, graphs, prints, etc., which involve a lot of processes, equipment and materials. A documentalist should therefore be well-equipped with these tools if he is to serve his clientele promptly and efficiently.

Reprographic techniques are varied, and the adoption of any one or a few of them depends on several factors, among which time and cost come foremost. Next, is the estimated demand for a document, whether a single copy or few or multiple copies will be required to serve the clientele. Here again, a documentalist should not be concerned with the present need only but also keep in view the anticipated demand too. A particular document may not have sufficient demand immediately, but its demand might grow in the near future on account of the nature and scope of the information contained therein. In that case, it is worth going in for multiple copies, which would save both time and money. Besides, decision has to be taken on the circumstances under which reproduction to be made is favourable for a micro or facsimile copy—the main two branches in which reprography is divided. Microcopy means a copy of the document in a highly reduced form, while facsimile, literally meaning a copy of the same size, also include a slightly bigger or smaller size copy than the original document provided the reproduced copy is of a readable size.

Micro-copying Methods

Microcopy or microfilm method has been known for more than a century. Messages in a miniature form were found to be communicated from Paris during its siege in winter of 1870-71. Afterwards the method became obsolete and was not in use for many years. The evolution of miniature cameras such as Leica, Retina and Contax led to the microfilm technique, which now occupies an important place in documentation. Reduction of bulk and weight which is the outcome of the microfilm technique is really advantageous in conserving storage space, thereby solving problem of accomodating vast store of knowledge. Furthermore, micro-techniques gained popularity on account of the economy it has brought in transmission of documents (in miniature forms), say, by air service. In spite of all such advantages, there is an apathy to use micro-form of documents because some magnifying appliances are required for reading, but such sentiments are now on the wane. Micro-reprography can be divided into two classes (i) Micro-transparency and (ii) Micro-opaques.

Micro-transparency

To meet the needs of a user who is far away or to provide a copy of a precious or fragile document, the transparent form of microcopy is used. In this method roll, strip or unitised transparent micro-films are used. A roll usually consists of 35 mm. wide microfilms of 100 ft. in length. Sometimes 16 or 70 mm. wide films are also used. Reproduction of back volumes of periodicals or other documents meant for storage are done by rolls. The roll has one disadvantage viz. a particular page of the document cannot be readily located.

Strip micro-films, usually 35 mm. wide and 23 cm. long, are used in documenting a few pages of a magazine of normal size, whereas unitised microfilms are smaller, just sufficient to cover a single or two pages. The latter are mounted on a rectangular aperture in a punched card.

These forms are meant for a single copy or short run. But when multiple copies are to be made, ribbon form of positive films are used to get a print from the master negative micro-film in roll forms. The positive film is much cheaper than the negative film. Hence it is economical to distribute identical copies of micro-documents to a number of users. Further economy has been effective by the introduction of diazo-coated and heat developed Kalvar films. Recently, a sheet form of micro-films, known as Microfische, is gaining much popularity, which is being used extensively for micro-recording of documents because it provides readily enlarged prints of readable size. Some commercial firms are marketing Microfische edition of back volumes of journals and out-of-print books.

Micro-opaques

Micro-opaques are photographically produced micro-cards on an opaque surface. They can also be produced by lithography following the principle of offset printing.

The equipments by which microfilms of document are made are essentially the same. The equipment consists of a microfilm camera on a stand where it can be moved up and down as well as sidewise, a table or a book holder on which to lay the originals and a suitable device to illuminate the document. Microfilm cameras have the same fittings as those of photographic cameras viz. an objective with a screen, a lock and shutter and devices to prevent double exposures and so forth. The arrangements for measuring the intensity of light, automatic advancing of the film after each exposure and controlling the exposure are provided. In the microfilm exposing machines, the motion of the originals

are synchronised with the advancing of films and the documents are rapidly photographed. After exposure, the films are passed on to a developing box wherein the microfilm is developed whilst it is wound on a spool. The spool with the film is immersed in a bath containing the developer solution. It is afterwards passed in succession through a fixing bath, an water bath and finally through the drying device. The films may be dried in air or in a drying cupboard.

After the master microfilm negatives are prepared, copies can be obtained either on to a positive photographic or a diazo film. When a roll film is to be copied, the master negative and the positive films in contact with each other pass continuously over rollers before a source of light in the copying machine. The exposed positive film is then developed, fixed and dried as before. The film is then ready for distribution. The readers can make out the things with the help of reading appliances, the simplest form of which is a magnifying glass. There are a number of microfilm reader appliances marketed by different firms, all of which are of foreign make except one manufactured by the Ordnance factory at Dehra Dun.

Much progress in this direction has been brought about by Minnesota Mining and Manufacturing Corporation of U.S.A., who are pioneers in introducing a machine called Thermofax Filmac microfilm reader-printer. This machine is provided with special devices for enlargement of micro-films on a special photographic paper under the trade name Thermofax. The exposed paper is processed automatically to enable the reader to get an enlarged copy by the simple push of a button. One point about storage of micro-films is that these materials have to be preserved in lead boxes and in safer places.

Facsimile Methods

There are two methods of producing facsimile copies. One is the Contact copying and the other Projection or Optical copying. Depending upon the type of photosensitive paper, the Contact copying method can be further subdivided into (i) silver-halide system, where photographic papers containing silver halide emulsions are employed; (ii) diazo or dyeline system based on the action of ultraviolet light on a class of diazo compounds; and (iii) the recently introduced thermographic process in which infrared radiations cause scorching effect upon a special class of materials on the print paper. Viewed from the form of light responsible for production of the print, the silver-halide system is classified under two heads, viz. reflex and transmission printing. Opaque and double-sided documents are very much suited to reflex method while transmission printing is meant for translucent one-sided document.

Reflex Printing: In the reflex method, photo-sensitive paper in contact with the document is exposed to the light source in such a way that light passes through the photographic material on to the document and the rays are then reflected back on it to cause the impression to be developed. Reflex copying or reflectrography therefore depends on the reflected beam of light. Thus in the first step, a negative containing laterally inverted image, which is also tonally inverted, viz. white in place of black and black in place of white, is obtained. The next step is to expose a second sheet of photo paper in contact with the negative just in the same manner as above and get a positive copy of the original. It is possible to produce several copies from one master negative, which lowers the reproduction cost since the cost of production of the negative is spread over subsequent copies. A copy can, however, be made on a transparent positive paper or positive film from which diazo or dyeline copies can be made to effect further economy in reproduction. The image on the negative paper can leave a positive print on a thin aluminium foil to be used for production of multiple copies in offset printing machine.

An improved technique has enabled to cut short the operation by passing the exposed negative paper in contact with a second sheet of photo paper through the developing machine. There, the two papers are passed through a pair of squeeze roller or a rubber lip the unexposed portions of the negative are thereby transferred on to the receiving paper. This transfer effect may either be a chemical—commonly known as diffusion transfer reversal (DTR)—or a physical transfer due to the presence of some kind of gelatinous material on the receiving paper; the latter is therefore termed as gelationous transfer reversal (GTR). Both the DTR or GTR processes have been perfected after the second World War.†

Another kind of development has resulted in production of a special kind of photo paper which is subjected to some exposure (of blue light) during manufacture. With such paper, direct printing by reflex method in one step is possible. An erect image of the document is no doubt obtained, but it is tonally inverted, i.e. white on black (if the original is black on white background) and black in place of white.

† by Agfa Co. of Germany and Gevaert Co. of Belgium.

Dr. E. H. Land in U.S.A. has succeeded in developing a technique called Polaroid-Land photograph, by which it is possible to give a completely processed and finished negative and a positive in true colours just 50 seconds after clicking a shutter.

Transmission Printing: As stated earlier, the impression in this method is done by transmitted light. This means that the photo-sensitive paper in contact with the document, which is either translucent or contains only one-sided matter, is subjected to exposure in such a way that the light transmitted through the document falls on the paper. The portions just opposite the written matters do not get any light. The print obtained is just like reflex contact printing in one step. The image is erect no doubt, but it is tonally inverted. By using special kind of paper, positive-to-positive copies can be produced in one step by using a strong yellow light. Thus, transmission printing saves both time and material in producing a positive copy in one step.

Diazo or Dyeline System

The diazo or dyeline system has superseded blue-printing, based on iron compounds and producing copies with white lines on a blue background. In this system, diazo or dyeline papers get the print on coming in contact with the document which should invariably be translucent or have one-sided matter only to transmit light through. But if the original is opaque or has double-sided matter, an intermediate master copy on a fairly thin, direct positive silver-halide paper may first be obtained by the reflex method. With this master copy, direct printing (by transmitted light) on the diazo paper can be done either by dry or wet development.

In the dry development method, the copy papers are coated with diazo compounds combined with some bonding components like phenols or amines. When these papers are exposed to strong ultraviolet light, the diazo compounds get deteriorated where light falls and those portions lose their capacity to form azo dyes. Those portions where no light falls retain the capacity of forming azo dyes; so on development the original is reproduced as a positive image. The formation of azo dyes is augmented by ammonia vapour, Hence the copy paper after exposure is kept in an ammonia vapour chamber for development. The copy is obtained dry.

In the wet development procedure, the copy paper is coated with diazo compounds only, without the bonding components of phenols or amines. The copy paper after exposure is sprinkled with the developing liquid composed of phenols or amines. In the developing machines the developing liquid is wiped off, and the copy comes out wet which is dried within a short time.

There is a third method of development‡ caused by heat only, which is called as Diazo-therm technique. It has yet to make its head up.

Usually the diazo or dyeline papers are not at all suitable for reflex printing. But the diazo material coated on an acetate film base (with an integral screen foil) is available in the market. It is meant for reflex printing. After exposure and development, the laminated foil is scraped off the paper, and this serves as the master or second original from which further copies using ordinary diazo paper can be obtained. The appliances by which ordinary diazo or dye line copies are produced are varied.

Thermographic Process

Chemical changes are responsible for the prints obtained in the silver-halide and diazo or dyeline system of reproduction. One method based on physical change known as Thermographic reproduction has been introduced under the trade name Thermofax.* In this system, paper is placed in contact with an original and subjected, as in the Reflex method, to exposure of infrared rediations when heat accumulates more on the darker portions of the original; this heat colours the Thermofax paper at those portions just in contact with the document thus producing a laterally inverted image of the original. Since the paper is very thin, the copy can be read easily from the back. This method is not suitable to copy the pages of books or bound volumes, but loose sheets can be done very easily. By this method, different colours, except light blue of the document, can be copied. However, this is the most simple and quickest method to get a copy within 2-4 seconds. Thermal copying methods are being superseded by electro-and magneto-copying techniques.

Xerography

One of the best electro-copying methods, Xerography is not entirely based on electrical phenomena but to some extent depend on heating effect also. In this system, an electrically charged selenium plate or charged plates with semiconducting coatings of zinc oxide or of recently introduced organic materials are rendered photo-sensitive. The image of the original document is projected on to the charged plate or coatings. The

‡ developed jointly by Copycat of U. K. and Bouchet of France.

* manufactured by Minnesota Mining & Mfg. Co., U.S.A.

charge leaks away from all parts where the light impinges and remains only on the image of the dark script of the text. Some oppositely charged resinous powder are sprinkled on the plate or coating, so that the powder adheres to the image portion. The powder image is then pulled off on to a plain paper which is placed over it and countercharged. Finally the powder is melted by heat by which a permanent impression is obtained on the paper**. Though the initial cost is very high yet the recurring material cost for obtaining copies of documents by this method is very low. Simpler and cheaper machines are now being developed and when this is achieved electrocopying method is destined to become popular.

In a technique almost similar to Xerography, developed by the Radio Corporation of America, the charged selenium plates or plates of semi-conducting coatings are replaced by a paper coated with photo-electric compound—zinc oxide with a resin binder. The powder image is developed on the exposed paper with a magnetic brush and need not be transferred as in Xerography.

Photronic Reproducer

It is an electrographic system, where charged atomised particles of ink mist are directed towards a sheet of paper in contact with a charged glass-metal laminate on which the image of a document is projected. The ink particles are deposited on the image areas giving a positive image of the document. The cost of such an equipment is also very high but the running cost of preparation of copies is very low.

Magneto-Copying Methods

Experiments are being conducted to introduce a new copying method based on magnetic principle. The method is so arranged that a thin sheet of iron becomes magnetised where it is in contact with the scripts of a document only. So when iron filings are sprinkled over it they adhere to those portions only. The iron filings can then be transferred on to a paper and fixed there. The advantage of the method lies in the fact that the magnetisation of the iron sheet is maintained for a prolonged time for which thousands of transfers to produce copies can be effected.

Projection Copying

Projection copying may be of bigger, equal to or smaller (within certain limits) than the original in size, and any of the systems of printing viz. silver-halide, diazo or thermographic can be adopted. The equipment necessary is generally a simple camera. First a negative is prepared, from which positive prints are taken. This two-step method may, however, be avoided with the help of an image erecting camera in which a right-angled prism is suitably placed in front of the lens. The mirror effect is thereby averted and a tonally inverted print of the original may thus be obtained in one step only.

Blow-back of microfilm images to near-original size is done by an enlarger, which is so designed that a sharp, uniformly illuminated image is produced on the photo paper. The image on this paper is developed, fixed and dried automatically with the touch of a button in the machine.

Duplicating Methods

Mechanical duplicating is now becoming common. There are three ways of doing it viz. (1) transfer printing from a master negative moistened with alcohol, (2) from wax stencil, and (3) by offset printing.

The first method is to have a mirror writing on a sheet of art paper with a special kind of carbon paper laid underneath it with carboned side upwards. The writing can be done by either a typewriter or hand with a hard ball pen keeping a hard surface underneath. This master copy can then be placed in a duplicator having cylindrical or flat bed with the mirror writing facing outwards. The paper is moistened with alcohol by a suitable arrangement. The colour of the writing is dissolved slightly and the writing is transferred on to a paper which is pressed in contact against it. The process can be repeated to get a small number of copies of heavy print or a greater number of lighter copies. The master copy can be made with carbon papers of different colours, and if appropriate colours are successfully placed copies of mixed colours can possibly be obtained. Any addition or correction can be incorporated on the master copy by cutting and pasting on to the desired portion. Master copy can also be preserved for future use.

Reproduction from Stencil

In this method, master sheets are made of stencil sheets, which are usually of Japanese silk paper or similar substitutes coated with wax. When these are typewritten or written by hand with a steel stylo, the the layer of wax is removed causing perforations permeable to ink. These duly cut stencil sheets serve as master and these are wrapped round a cylinder of fine

** The equipment is manufactured by Xerox Inc. (formerly Haloid Inc.) in U.S.A. and Rank Xerox in U.K.

mesh through which ink is spread first on master stencils and through them on to copy papers when pressed against them. The machine may be hand-operated or electrically-driven. Usually 500 copies can be made from each stencil. Gestetner photoscope stencils can give master copy with photo projection whereas electronic stencil cutter give master copy by electrical scanning of the document.

Offset Printing

An offset printing machine consists of three moving drums contiguous to each other. The master copy is made up of aluminium foil on which the original is typed or hand-written using a special ribbon or pencil so that only the marked portions will take up ink. When this master copy is wrapped round the first drum and moistened with ink, it leaves a laterally inverted impression on the rubber band of the second drum when the machine is switched on to run. The impressions on rubber band of the second drum are again transferred to the copy paper carried by the third drum. The aluminium foil with a special photo-sensitive material on it may have the original written on it by photo projection and can serve as a master for printing when it is called photo offset master. This is in fact advantageous, as no error can creep in the copy, since it is obtained photographically from the document.

Before a particular method is applied, a documentalist should examine the original document meant for reproduction on the following points: He should ascertain whether a particular method or a combination of methods would be suitable. First thing to be examined is whether the document is on an opaque or translucent paper, next whether the reading matter is double or single-sided. These would tell whether reflex or direct contact printing could be applied. Next, whether the document is in loose sheets or in bound volumes, its size (whether small or big), the number of pages—single, a few or many—the urgency, meaning thereby the availability of time, number of copies required keeping in view the immediate as well as anticipated demand, usefulness at present, and in future to gauge the longevity of the reproduced copy and tolerance regarding quality (sharp or blunt scripted reproduction), etc. Above all, the economy involved in reproduction demands a special attention to perform the job within the budget in hand. It may be that immediate production of a copy may be too cheap but installation cost of the equipment is extremely heavy as is the case with Xerography. So, if by calculation it is found that the heavy cost of installation is recoverable within 2 to 3 years on the basis of lesser reproduction cost, then such an equipment is worth having. Otherwise one has to go in for higher costing procedures for obtaining copies which would however incur less installation cost.

It is evident that reprography is a specialised job. It demands comprehensive knowledge and vast experience in this field on the part of a documentalist to perform the job effectively, economically and efficiently.

Acknowledgement

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Solubility of Arsenic Trioxide in Aqueous Ammonia at 40° and 50°C

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Solubilities of arsenic trioxide in aqueous solutions of ammonia have been determined at 40° and 50°C in an apparatus specially designed to prevent leakage of the gaseous component from the solution.

In factories producing ammonium sulphate, trivalent arsenic is used as an inhibitor of corrosion of stainless steel in hot dilute sulphuric acid. The inhibitor is added as a solution of arsenic trioxide in caustic soda or in aqueous ammonia. It is preferable to use the latter solvent as it is available readily in the factory itself at a cheap price. The solubility of arsenic trioxide in this solvent has been determined at 30°C but not at higher temperatures.[1] In the present study the solubility of arsenic trioxide in aqueous ammonia of different concentrations has been determined at 40° and 50°C as these values are required for the preparation of inhibitor solutions in the plants.

A special apparatus has been designed which will be suitable for solubility studies in which equilibrium concentrations are likely to be affected due to possible leakage of a gaseous component, like ammonia, from the system (Fig. 1). The apparatus can be placed inside a thermostat for carrying out experiments at constant temperatures. The use of an internal stirrer is eliminated, and the arrangement is made for the rotation of the apparatus by an A.C. motor.

The solubility vessel C is made of pyrex glass, having a diameter of about 60 mm. Two side tubes D_1 and D_2 are joined to B_{10} standard joint sockets through pyrex glass stopcocks S_1 and S_2 and are used to discharge the solution from the upper end and the magma from the lower end respectively. The third side tube D_3 with stop-cock S_3 is used for connection with outside atmosphere, when necessary. The mouth of the vessel is closed tightly by a grooved rubber stopper.

The vessel C is made to rotate by an arrangement which comprises two parts, viz, A and B. The upper portion of A is made up of a brass rod having a diameter of about 50 mm. with a cavity (of 14 mm. diameter and 50 mm length) at the centre and fitted on a heavy stainless steel base. The base is fixed by means of binding screws in the thermostat. The part B is a brass platform with an arrangement for holding the solubility vessel. A brass rod protruding from it fits inside the cavity

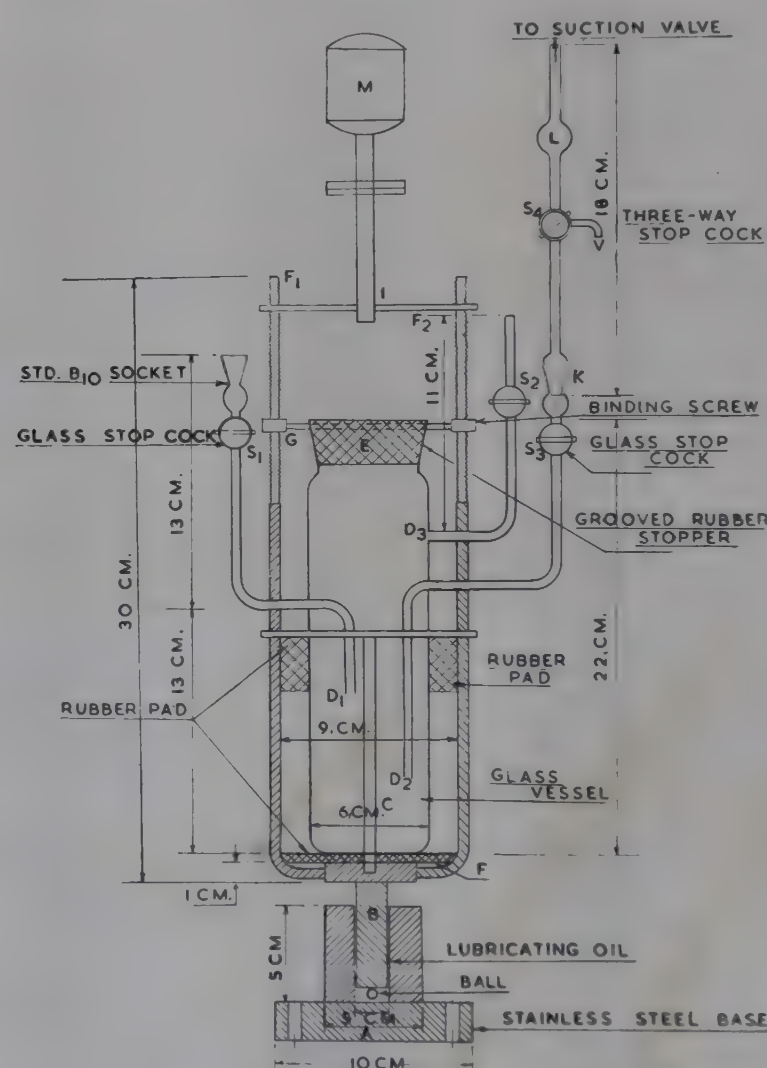

Fig. 1. Solubility Apparatus.

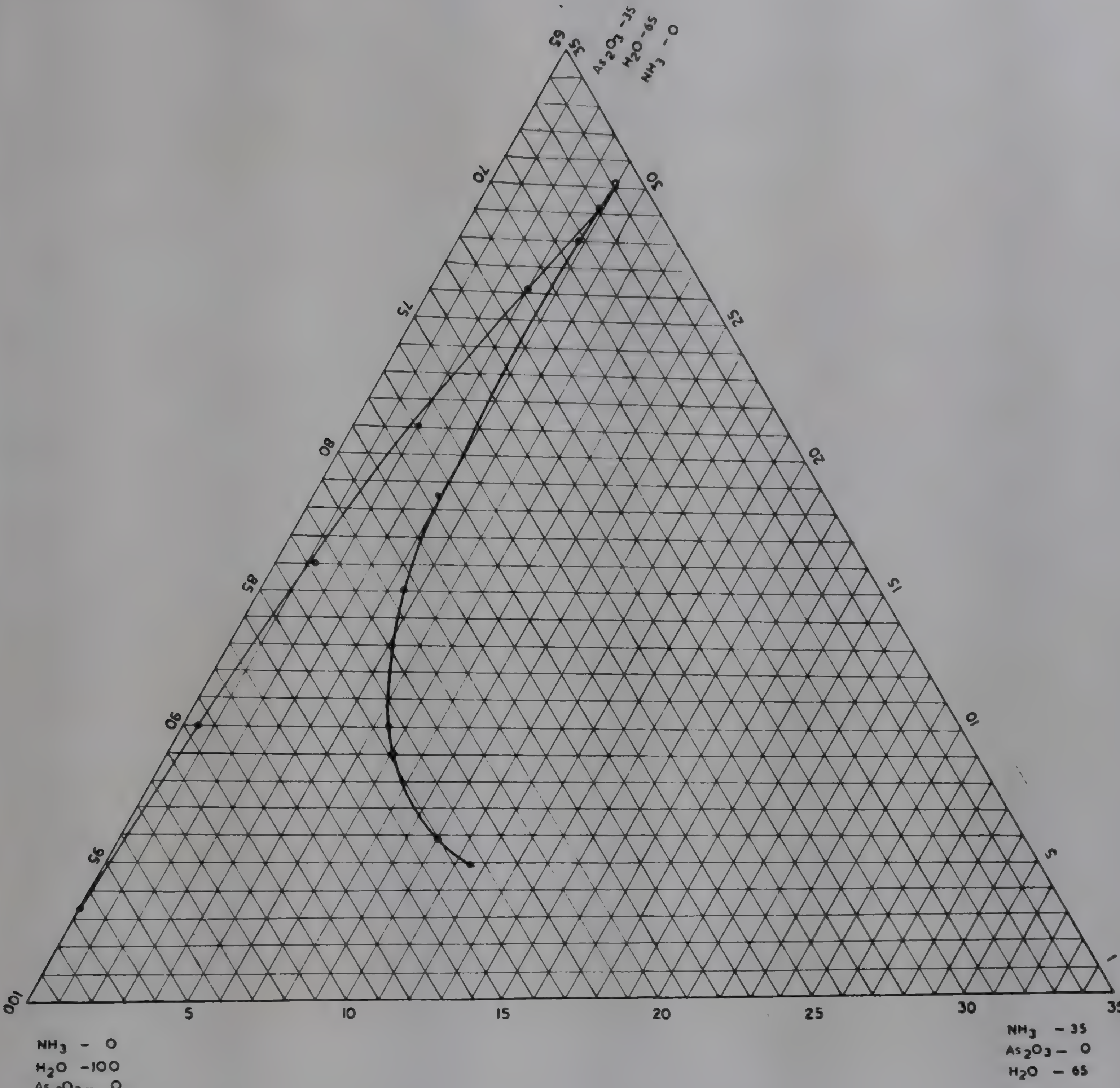

Fig. 2—Diagram for NH_3-As_2O_3-H_2O System at 50° ± 0.1°C.

TABLE 1—SOLUBILITIES OF ARSENIC TRIOXIDE IN AQUEOUS SOLUTIONS OF AMMONIA

(Values expressed as g./100 g. of saturated solution)

	Temperature 30°C			Temperature, 40°C*			Temperature, 50°C*		
	NH_3	As_2O_3	Solid Phase	NH_3	As_2O_3	Solid Phase	NH_3	As_2O_3	Solid Phase
1.	0	2.26	As_2O_3	0	2.71	As_2O_3	0	3.35	As_2O_3
2.	1.41	10.98	"	1.75	13.66	"	1.32	13.86	"
3.	2.78	20.49	"	2.40	20.10	"	2.32	22.56	"
4.	2.86	21.17	"	3.40	25.10	"	2.84	25.05	"
5.	2.88	18.43	NH_4AsO_2	3.58	26.02	"	3.47	27.31	"
6.	3.13	12.30	"	3.71	13.43	NH_4AsO_2	3.67	27.96	"
7.	3.91	7.63	"	4.03	11.60	"	3.90	29.20	"
8.	6.95	4.72	"	4.72	10.55	"	4.15	18.82	NH_4AsO_2
9.	9.63	3.20	"	4.70	9.00	"	4.86	14.70	"
10.	14.28	2.16	"	5.74	7.77	"	5.30	12.47	"
11.	—	—	—	8.67	5.01	"	7.35	8.92	"
12.	—	—	—	12.10	3.35	"	7.91	6.53	"
13.	—	—	—	—	—	—	9.49	6.87	"
14.	—	—	—	—	—	—	10.58	5.79	"
15.	—	—	—	—	—	—	12.73	4.69	"

* Data obtained in the present study

in part A. The dimensions are indicated in the figure. Two thick wires F_1 and F_2 in part B are connected with an A.C. motor by an arrangement I. The solubility vessel with its contents is placed on the platform in part B and is fixed properly by means of rubber pads. The mouth of the vessel is closed by a grooved rubber stopper, on which pressure is applied by means of a looped thick brass wire and binding screws G thus making it leakproof. The apparatus is rotated by a motor and a ball bearing arrangement at the base as shown in Fig. 1.

In determining the solubilities of arsenic trioxide in aqueous ammonia of different concentrations, excess of solid was kept in contact with the liquid till the equilibrium was reached. Ammonia was estimated in a weighed amount of the solution by Kjeldahl distillation method and trivalent arsenic by the standard iodometric method. The identity of the solid phase present at equilibrium was established by Schreinmaker's wet residue method[2].

The results of solubility determinations at 40° and 50°C are given in Table 1. The data obtained at 50°C have further been plotted on a triangular diagram (Fig. 2). The values at 30°C, as determined earlier, are also shown in the table 1 for comparison. It will be observed that at all these temperatures, the solubility of arsenic trioxide goes on increasing with increase in the concentration; the decrease starts when the solid phase at equilibrium charges to ammonium arsenite from arsenic trioxide. As the temperature increases, the maximum amount of trivalent arsenic that can be kept in solution also increases but the point of maximum solubility shifts to a solution having a higher concentration of ammonia.

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Desensitizers for Ammonium Nitrate

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Increased stability of ammonium nitrate by the addition of 1 per cent each of urea, calcium carbonate and zinc oxide have been investigated thermogravimetrically and by pH determination of the evolved gases. The latter technique appears to provide a reliable index to the stability of ammonium nitrate. Explanations have been put forward on the role of these additives. Urea appears to be the most effective inhibitor, examined so far.

Chemically pure ammonium nitrate does not decompose at ordinary temperatures. When heated without confinement it dissociates soon after it melts at 169°C into ammonia and nitric acid, and starts evolving nitrous oxide and water. The former reaction is highly endothermic and the latter weakly exothermic, and therefore the system shows little tendency towards self-accelerating decomposition. When heated under confinement, the situation changes and self-accelerating decomposition may set in on account of suppression of endothermic dissociation of the salt and occurrence of highly exothermic reactions. The temperature under such conditions may rise rapidly till an explosive rate of decomposition is attained[1,2]. Conditions of confinement and temperature stated as essential for the explosion of pure ammonium nitrate are 100 Kg/sq.cm. and about 300°C respectively[3,4]. These conditions are not likely to be attained under normal conditions of handling and storage. But a dangerous situation may arise if the salt gets contaminated with some of the impurities. The carbonaceous material such as jute, paper and wooden crate (dunnage)—most likely contaminants—sensitize ammonium nitrate and bring down the limiting conditions of explosion to a level that may prove dangerous. Metal strips of copper, brass and powdered metals especially zinc cause self-sustained exothermic reactions to occur at 173°, 167°, and 117°C respectively[5]. Magnesium reacts violently with ammonium nitrate[6]. Chlorides — even in traces—fuel oil, petroleum residues and oxidizing agents such as chromates also sensitize ammonium nitrate[4].

Ammonium nitrate is a concentrated nitrogenous fertilizer containing nitrogen both in nitric and ammoniacal forms, and its efficacy as a fertilizer is well-established. Hazards associated during its storage and handling are eliminated by diluting it with 40 per cent of limestone or chalk.[5] Addition of limestone decreases its nitrogen content and prevents free acidity to develop. The reaction of ammonium nitrate with calcium carbonate is an endothermic one and prevents further increase of temperature. Dilution of ammonium nitrate, however, increases considerably the cost of the fertilizer per unit weight of nutrient.

Need was, therefore, felt to study desensitizing influence of some substance, added in small amounts, with a view to ascertain whether such additives can sufficiently stabilize ammonium nitrate so as to render the product in a more concentrated form. The present communication is the result of preliminary study on this problem. The stability of ammonium nitrate has been evaluated by pH determination of evolved gases and results compared with these obtained from thermogravimetric method that determines weight loss as a function of temperature.

The role of urea as a stabilizer was first discovered as early as in 1922 by Findlay and Rosebourne[7] who found that it prevented the development of free nitric acid in ammonium nitrate and thus made it immunne to the sensitizing influence of wood meal and starch. Braconier and Delsemme[8] found that the addition of 2 per cent calcium carbonate increased the explosion threshold to 320°C and 150 Kg/sq.cm. Influence of zinc oxide on the acidity of the melt was investigated potentiometrically by Rozman[9], who showed that zinc oxide prevented acidity to develop in the ammonium nitrate melt.

Gases evolved during thermal decomposition of pure ammonium nitrate are nitrous oxide, ammonia, water and nitrogen. The latter is present in small proportion—nearly 2 per cent upto 260°C, the percentage is consider-

ably more at higher temperatures. Nitrogen dioxide and nitric oxide are also present though in traces[10] i.e. 0.001 per cent of each between the temperatures 220 — 260°C. Extremely low percentage of nitrogen dioxide in the evolved gases is surprising in view of the fact nitric acid is known to decompose as follows:

$$4HNO_3 \longrightarrow 4NO_2 + 2H_2O + O_2$$

This may be so because ammonia is known to react vigorously with nitrogen dioxide evolving nitrogen and water.

$$2NO_2 + 2NH_3 \longrightarrow NH_4NO_3 + N_2 + H_2O$$

As the temperature is further increased the proportion of nitrogen dioxide increases and exothermic reactions prediominate over the endothermic dissociation of the salt.

$$NH_4NO_3 \rightleftharpoons NH_3 + HNO_3$$

This is significant with respect to the stability of ammonium nitrate as it was observed that explosive decomposition was always accompanied with the liberation of oxides of nitrogen at the expense of ammonia.[8]

pH of evolved gases would obviously depend on the proportion of ammonia to acid components, viz. oxides of nitrogen and vapourized nitric acid. When ammonium nitrate was heated at a constant rate and pH of the evolved gases determined by pH paper, it was found that the gases continued to be alkaline up to a certain temperature above which the gases became acidic in character. This transition took place abruptly. The addition of calcium carbonate, zinc oxide or urea increased the transition temperature to varying extent (Table 1). A change in the nature of gaseous decomposition products from basic to acidic may be interpreted as the tendency of the system to change from reactions that are overall endothermic to exothermic ones, which under certain conditions may give rise to self-sustained decomposition. In the case of pure ammonium nitrate the transition from basicity to acidity is 245°C. It may be recalled that Keenan[11] during differential thermal

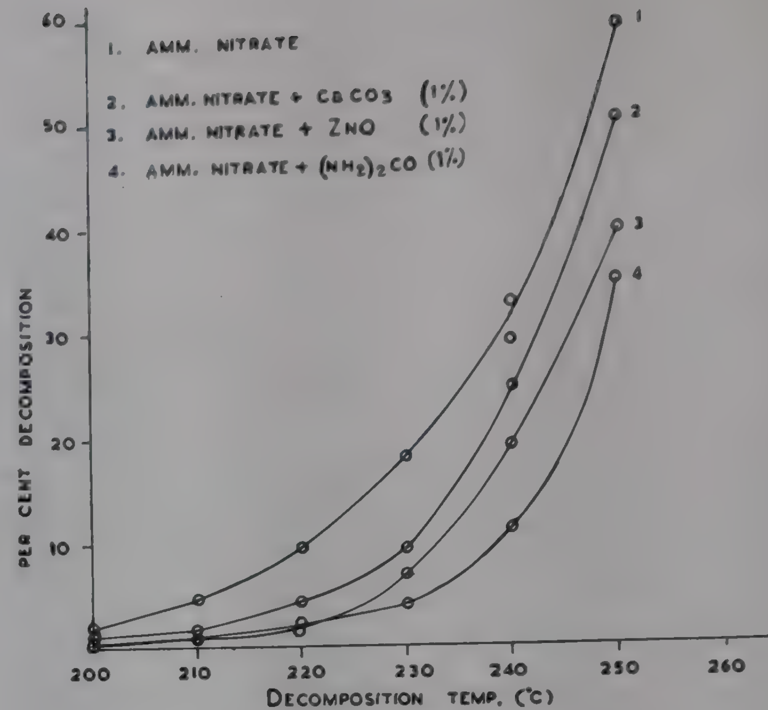

Fig. 1—Decomposition of Ammonium Nitrate.

analysis of ammonium nitrate obtained a weak maxima at 245°C.

The increase in the temperature of transition was found to be significant in the case of urea and zinc oxide but smaller increase was observed with calcium carbonate. Similar trend is observed from thermogravimetric studies as shown in the graph (Fig. 1). Urea, zinc oxide and calcium carbonate inhibit the decomposition of the salt. Urea is the most effective and calcium carbonate the least as inhibitor.

Valey[12] found that the rateof decomposition of ammonium nitrate into nitrous oxide and water was dependent not only on the mass of the salt undergoing decomposition but also on the proportion of free nitric acid present. Addition of acid at 200°C was found to increase 200 times the rate of decomposition of ammonium nitrate[13].

Urea decomposes with evolution of ammonia soon

TABLE 1—pH VALUES OF EVOLVED GASES

Sample	Heated to °C										
	210	220	240	245	250	255	260	265	270	275	280
Ammonium Nitrate	9	9	8	6	6	4	3	2	2	2	2
Ammonium Nitrate + 1% $CaCO_3$	9	9	9	9	2	2	2	2	2	2	2
Ammonium Nitrate + 1% $CO(NH_2)_2$	9	9	9	9	9	10	10	10	4	4	4
Ammonium Nitrate + 1% ZnO	9	9	9	9	9	9	9	10	2	2	2

after it melts at 132°C and the decomposition is fairly rapid at 150°C. The stabilization of ammonium nitrate is achieved by neutralization of the acidity in the melt by liberated ammonia and consequential decrease in the rate of decomposition. The results indicate that urea is able to stabilize even at higher temperature and fall in pH at transition is not as much as in the case of zinc oxide and calcium carbonate. This may be due to its increased stability in presence of ammonium nitrate as shown by the potentiometric studies of urea and ammonium nitrate system[14], with the result that the release of ammonia is slow and steady even at higher temperatures.

Zinc oxide reacts with ammonium nitrate melt to form di-and tetraammine zinc nitrates[9,15] as follows:

$$ZnO+2NH_4NO_3=Zn(NH_3)_2.\ (NO_3)_2+H_2O$$

$$ZnO+2NH_3+2NH_4NO_3=Zn(NH_3)_4.\ (NO_3)_2+H_2O$$

Zinc ammine nitrates tend to loose ammonia slowly as the temperature is increased above 200°C and the ammonia evolved neutralizes the melt as in the case of urea. Calcium carbonate, on the other hand, decomposes ammonium nitrate and evolves ammonia, carbon dioxide and water. The reaction occurs at a lower temperature and releases ammonia spontaneously rather than in a controlled manner. Calcium carbonate is, therefore, not as effective as urea or zinc oxide as a stabilizer for ammonium nitrate.

It is most significant that these additives prevent ammonium nitrate from the sensitizing influence of carbonaceous materials and chlorides[7,16], since contamination by such substances may prove dangerous. Further studies on these aspects are necessary and therefore being continued.

The authors thank Sri N. G. Sinha for his help in conducting experiments.

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Determination of Total Pyridines and Quinolines in Ammoniacal Liquor by Ultraviolet Spectrophotometry

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An ultraviolet spectrophotometric method for determining the total pyridines and quinolines in high temperature coal carbonization liquor has been described. The bases are extracted finally by specpure iso-octane solvent after treatment of the liquor, and the absorbances are measured at 260mμ and 316.5 mμ respectively. The amount of total pyridine and quinoline bases were determined. The preparation of specpure iso-octane is also discussed.

Low boiling pyridine bases, such as pyridine, α-picoline, β-picoline, γ-picoline and similar other compounds are important raw materials for the preparation of valuable drugs and pharmaceuticals. Since the coke-oven by-products, like tar, ammoniacal liquor and benzole, are important sources for these compounds, it is of interest to develop suitable methods for their recovery. In order to recover pyridine and quinoline bases from coke-oven liquor, it is important to determine their presence as accurately as possible.

Barker et al[1] have described the ultraviolet spectrophotometric method for determining total phenols and total monohydric phenols in the ammoniacal liquor. Chang and co-workers[2] have discussed a method of determining total pyridines and quinolines in tar by ultraviolet spectrophotometer and actually determined individually the spectra of a number of these bases.

The determination of total pyridines and quinolines in coke-oven liquor has also been carried out by ultraviolet spectrophotometry and the results compared with other methods of determination.

Experimental

A large volume of ammoniacal liquor from the coke-oven plant of Sindri Unit was acidified with concentrated hydrochloric acid and kept under carbon dioxide atmosphere to prevent the atmospheric changes in liquor constituents. The liquor was filtered and concentrated to a small volume. This concentrated liquor was made just alkaline by adding sodium hydroxide and then shaken several times with ether. The ether-soluble part which now contained mainly basic and neutral substances was again shaken with 50 ml. of 10 per cent v/v sulphuric acid. 25 ml. of the acid-extract was then shaken well twice with 25 ml. of specpure iso-octane prepared in this laboratory to remove the neutral material, if any. This treated acid solution was made up to 25 ml. with 10 per cent v/v sulphuric acid solution as there was some volume distortion. From this acid solution 2 ml. was poured into a beaker containing a little water, and the solution was maintained at pH-12 by adding sodium hydroxide pellets and its volume again adjusted to 25ml. 5 ml. of this solution was extracted three times with 10 ml. of specpure iso-octane and collected in a lot, and its ultraviolet spectrum were determined by Cϕ4 spectrophotometer.* The optical densities were read at 260mμ and 316.5 mμ, and by the formulae (given below) the total pyridines and quinolines were determined.

$$\text{Total Quinoline,} \quad Q = \frac{{}^{A}316.5\ m\mu}{15.95} \times F_1 \times F_2$$

$$\text{Total Pyridine,} \quad P = \frac{{}^{A}260\ m\mu - \dfrac{{}^{A}316.5\ m\mu \times 23.24}{15.95}}{21.25} \times F_1 \times F_2$$

where F_1=Dilution factor for final iso-octane extract (Here F_1=1 in the above procedure), and F_2=Dilution factor for the sample (F_2=3.75 in the above procedure)

${}^{A}260$ mμ and ${}^{A}316.5$ mμ are the absorbances at 260mμ and 316.5 mμ respectively.

* Russian make

Preparation of Specpure Iso-octane: The absorbances of the iso-octane against water was found to be considerable, showing thereby impurities present in it. The pure solvent was distilled under controlled temperature and the fraction boiling between 97° to 100°C was collected. This distilled solvent was passed through activated silica gel of 200 mesh (B.S.) packed in a chromatographic column. The eluted fraction of iso-octane had negligible ultraviolet absorbances.

Results

A number of samples of high temperature coal carbonisation liquor from the Sindri coke-oven plant were analysed, and the average values of pyridine and quinoline bases from different batch analyses are recorded (Table 1).

TABLE 1—PYRIDINE & QUINOLINE IN SINDRI COKE-OVEN LIQUOR

Sample No.	*Total Pyridine, g./l.*	*Total Quinoline g./l.*
1	0.115	0.080
2	0.123	0.083
3	0.110	0.070

Discussions

The individual ultraviolet spectra of pyridine and quinoline are found to be steep and narrow in the absorption band of each of the compounds. The average absorption maxima[3,4] of the pyridines are at 260 mμ and those of quinolines at 316.5 mμ. Since the presence of pyridines and quinolines in the high temperature carbonization liquor of Sindri coke-oven plant is very little, attempts are being made for their recovery by the application of column chromatographic techniques, which will be communicated later.

Acknowledgement

The authors are thankful to Dr. B. K. Banerjee of the Physical Wing for providing facilities for carrying out work on ultraviolet spectrophotometer.

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Testing of Gas Mask Cannisters

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Gas mask cannisters have been tested by an apparatus which has been designed to simulate human breathing cycle.

In the fertilizer industry gas masks have often to be put on by operating personnel working in atmospheres containing carbon monoxide, ammonia, etc. The efficacy of the gas mask cannisters containing active chemicals has sometimes to be checked before a consignment is approved for being issued to the workers. An apparatus, suitable for this purpose, has been designed so that it can simulate the human respiration cycle. This apparatus can also be used for testing cannisters in gas masks meant for protection against gases other than ammonia.

The volume of air breathed in and out during quiet respiration[1] is 400-500 ml. per respiration. In a minute, a normal human being respires 14-16 times; this corresponds to a maximum inspiration rate of four litres per minute. When the air is breathed in, the lungs are inflated to a certain maximum pressure (+7 mm.Hg.), while in the reverse process the pressure in the lungs is reduced to a certain minimum value (−5 mm.Hg.), above and below which the lungs may cease to work. These factors have been taken into consideration in constructing the

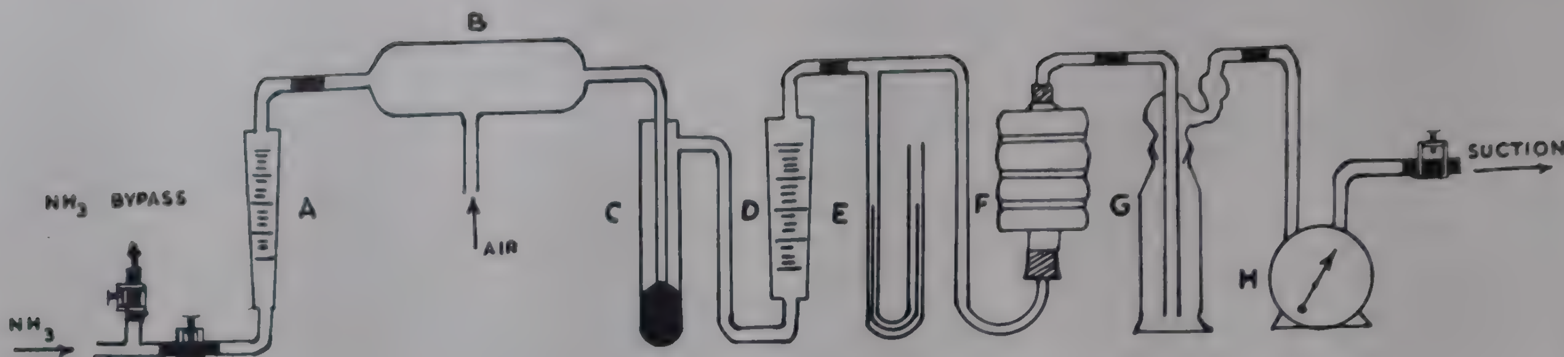

Fig. 1—Apparatus for Testing Gas Mask Cannisters

apparatus. Arrangement has been made to control automatically the total volume of air sucked in through the cannister to a value of 4 l./min. which is the maximum during inspiration; the maximum suction pressure is also controlled automatically at 12 mm. of mercury, which corresponds to the range −5 mm. to +7 mm. mercury during respiration.

Description of the Apparatus

Ammonia gas is drawn from a cylinder, and its flow at the cylinder side is controlled by a needle valve fitted with flow and pressure regulators (Fig. 1). The gas is passed through a rotameter (A) for measuring the final volume of ammonia going to the cannister. A by-pass arrangement at the inlet side is made to control the fluctuation of flow, if necessary. Ammonia gas then goes to a mixer (B) where air is drawn in and mixed up with it. The mixed gas is then passed through another rotameter (D) of suitable capacity where its final volume is measured.

From the total flow of the mixed gas and the flow of ammonia, the actual percentage of ammonia in air is calculated. The air which is passed is free, and the percentage of ammonia in it is maintained at about 2 per cent by volume. The gas mixture is then bubbled out through a gas bubbler (G), via mercury trap (C), rotameter (D) and gas cannister (F) and is passed through the wet gas meter (H) to the suction. The purpose of using the mercury trap is that during the deadp eriod the gas mixture may not flow to the cannister and is vented out through the air inlet side of the mixer. The flow of air or gas mixture and the final pressures are controlled by a manometer (E), through a relay system (J) (Fig. 2)

The manometer consists of a U-Tube (I) of 8-10 mm. bore diameter and about two feet high with a side tube (Fig. 2). About two-thirds of its lower limbs are made of capillary tubes (L) of 0.5-0.75 mm. bore diameter. Through the open ends of the vertical limbs, two electrodes (K) are inserted, the heights of which can be adjusted by screwing. The electrode at the left limb is fitted tightly to it during suction, and only the side tube at this end is connected to the suction line.

The tip of the electrode is kept slightly above the level of mercury. The other electrode at the right limb is fitted loosely and goes well inside the level of mercury. A layer of paraffin is placed on both sides of mercury column, so as to avoid oxidation during make and break of the circuit when a minute sparking occurs occasionally. The two electrodes are connected to the relay system (J), which also operates the suction pump. The choice of capillary—its bore diameter and height—was made after several trials.

A pilot lamp is placed in series with the relay system to indicate the continuity (or discontinuity) of the circuit and hence the running period in the process.

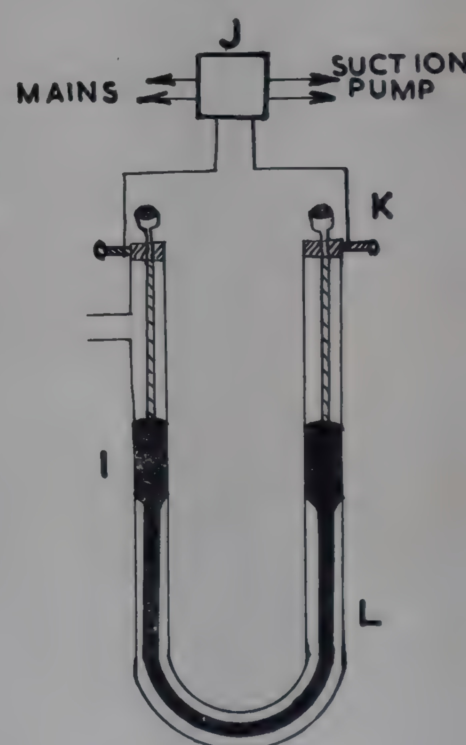

Fig. 2—Relay System for Flow of Air or Gases

Experimental Procedure

The initial setting up of the apparatus is done by passing free air only and noting the rise in the column of mercury, flow of air per period, total number of periods in each minute and time lag. The flow can be adjusted by the suction pressure of the suction pump either by a by-pass system in the suction line or by the suction pump itself whose suction can be varied by a control knob. To adjust the time lag between two running periods, the suction line connected to the side tube of the manometer is throttled slightly so that the rise and fall of the mercury column can be delayed with the operation of the suction pump. The flow of gas mixture is kept at 400-500 ml. per running period, and there are 10 to 8 running periods every minute so that the total flow of gas mixture per minute is about 4 l. The levels of mercury column in the two limbs are kept initially at the same height, and the markings are noted. As soon as the motor starts operating, the level of mercury in the left limb goes up gradually and short circuits the relay, which stops automatically the suction pump. Due to the residual suction, mercury rises to a slightly higher level and then starts falling,. It goes past its initial level and adjusts to a slightly lower one, and the suction pump starts working again. The total suction pressure is obtained from the difference between the lowest and the highest levels which are reached by the mercury column; this is about 12±2 mm.

Results and Discussion

The cannister, nos A, B and C, were received for test from the fertilizer factory at Nangal, while D and E were from the stock used at Sindri fertilizer factory (Table 1). Air containing two per cent by volume of ammonia was passed through the cannisters under test.

TABLE 1—TESTING OF AMMONIA GAS MASK CANNISTERS

[*Air containing 2% NH_3 (by vol.) was passed*]

Cannister No.	*Gas Flow Rate, l./min.*	*NH_3 in Exit Gas, ppm.*			
		1st 30 min.	*2nd 30 min.*	*3rd 30 min.*	*4th 30 min.*
A	5.5	14	—	—	—
B	4.0	21	24	—	—
C	,,	20	24	19	129
D	,,	20	14	19	101
E	,,	21	13	14	27

The maximum allowable concentration of ammonia in air for the safety of a human being is stated to be 100 ppm. for prolonged exposure and 300-500 ppm. for 1 hr.[2] It will be seen from the results that ammonia in exit gas from Cannister Nos. C, D, E was within 25 ppm. for the first three periods of 30 minutes (Table 1). The cannisters A and B were tested for 30 and 60 mins. respectively, and during these periods ammonia in the exit gas did not exceed 25 ppm. There were sudden increases in ammonia concentrations in the exit gases from cannister C and D to values 129 and 101 ppm. respectively for the fourth period of 30 min, but even these values where within the limit of 300-500 ppm. of ammonia for one hr. exposure. Thus, under the present conditions of test all the ammonia gas mask cannisters seem to work satisfactorily.

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Technical Digests

Revivification of Spent Iron Oxide Catalyst

Iron oxide is commonly used for the desulphurization of industrial gases like coal gas, water gas, producer gas, etc. In the process, hydrogen sulphide of the gas combines with the oxide forming iron sulphide, which gets converted to elemental sulphur. The iron oxide left is reused for sulphur removal. But after repeated use, sulphur concentration in the spent iron oxide gets high, thus rendering the latter unsuitable for further use.

A process has been developed in this laboratory* by which the spent oxide, unsuitable for further use, can be revivified yielding, in addition, sodium thiosulphate as a by-product.

The process is as follows: The spent oxide is treated in a steam-jacketted digester with water under constant agitation to maintain it in the form of a slurry. Commercial sodium sulphite is then added until the ratio of sulphur (in the spent oxide) to sodium sulphite is about 1.0 - 1.5, and that the concentration of sulphite in the slurry is in the range 25 to 50 per cent (w/w). The digestion is continued for about 2 hours at 60° - 95°C after which the material is cooled and filtered. The insoluble portion is washed with water until free from sulphur compounds and then air-dried. The revivified iron oxide, thus obtained, is as active as the free iron oxide.

The filtrate, consisting mainly of sodium thiosulphate and some unreacted sulphite, is purified by passing through a bed of active carbon. The liquor is then concentrated, cooled and crystallized. The crystalline thiosulphate, thus obtained, is of photographic quality.

Coal for Korba Fertilizer Project

The selection of Korba (M.P.) as the site for a fertilizer plant is based mainly on its location in a coal-bearing area. The Korba coalfield, lying in the lower Hasdeo Valley in the Bilaspur Dist. and covering an area of about 200 square miles, has two main horizons. Bore hole records and other outcrops reveal the presence of several seams of thickness 6 to 120 ft. The workable seams are: (*i*) a lower horizon containing a seam of an average thickness of 5 ft.—Lower Ghordewa—of good quality (ash 15 per cent on air-dried basis) and two other seams varying from 4 to 10 ft in thickness and generally of less superior quality in Rajgamarh sector (Fig. 1), and (*ii*) an upper horizon containing a thick seam (84 ft) of inferior quality commonly known as Jatraj seam (ash 28-43 per cent on air-dried basis). The total reserves of good quality coal in this area are 60 million tons and those of inferior grade 200 millions.

Exploration carried out by the Indian Bureau of Mines during 1957-58 indicated the existence of 4 seams of varying thicknesses in the Rajgamarh area. In many cases, the seams have thinned down to less than 1 ft and their ash content varies widely—9 to 35 per cent. At some places only one seam has been met, while at other places all the four have been found. The Central Fuel Research Institute has divided Rajgamarh coalfield in four areas and estimated the reserves as 77 m.tons. According to CFRI*, the average thickness of No. 2 seam (Rajgamarh area) is of the order of 5 ft, with a more or less ash content around 20 per cent.

The coal is required for gasification and also for steam generation. For use in gasification, it has to be of uniform quality, particularly in ash content. In order of have a clear idea about the quality of the coal, the National Coal Development Corporation were advised by this Division† of FCI Ltd. to sink bore holes in particular area of No. 2 seam where the NCDC want to open up their mines. The bore hole cores were than tested.† In all 33 bore holes were sunk, of which 12 were sunk by contractors.

The No. 2 seam was met at depths 97 to 677 ft in different bore holes (Fig. 2). It is almost free from shaly bands. Its thickness varies between 1 ft 11 in. to 8 ft 8 in., and moisture and ash contents between 5 to 8.9 and 9.1 to 17.4 per cent on air-dried basis respectively. The other characteristics are as follows: volatile matter between 27.6 and 32.5 per cent; calorific value 10150-11920 Btu/lb on air-dried basis. The coals are non-caking having sulphur content, 0.4 to 0.82 per cent, except in three samples (sulphur 1.69 - 2.72 per cent).

* 'A Process for Revivification of Spent Iron Oxide and Making of Sodium Thiosulphate as a By-Product' Indian Pat. No. 80428 (Inventors: Dr. K. R. Chakravorty, S. P. Sen and N. B. Bhattacharyya).

* Unpublished Report.

† A Survey of the Coal Seams of Rajgamarh Field (Korba) for their Utilization in the Fertilizer Factory at Korba, P&D. Division, FCI Ltd.

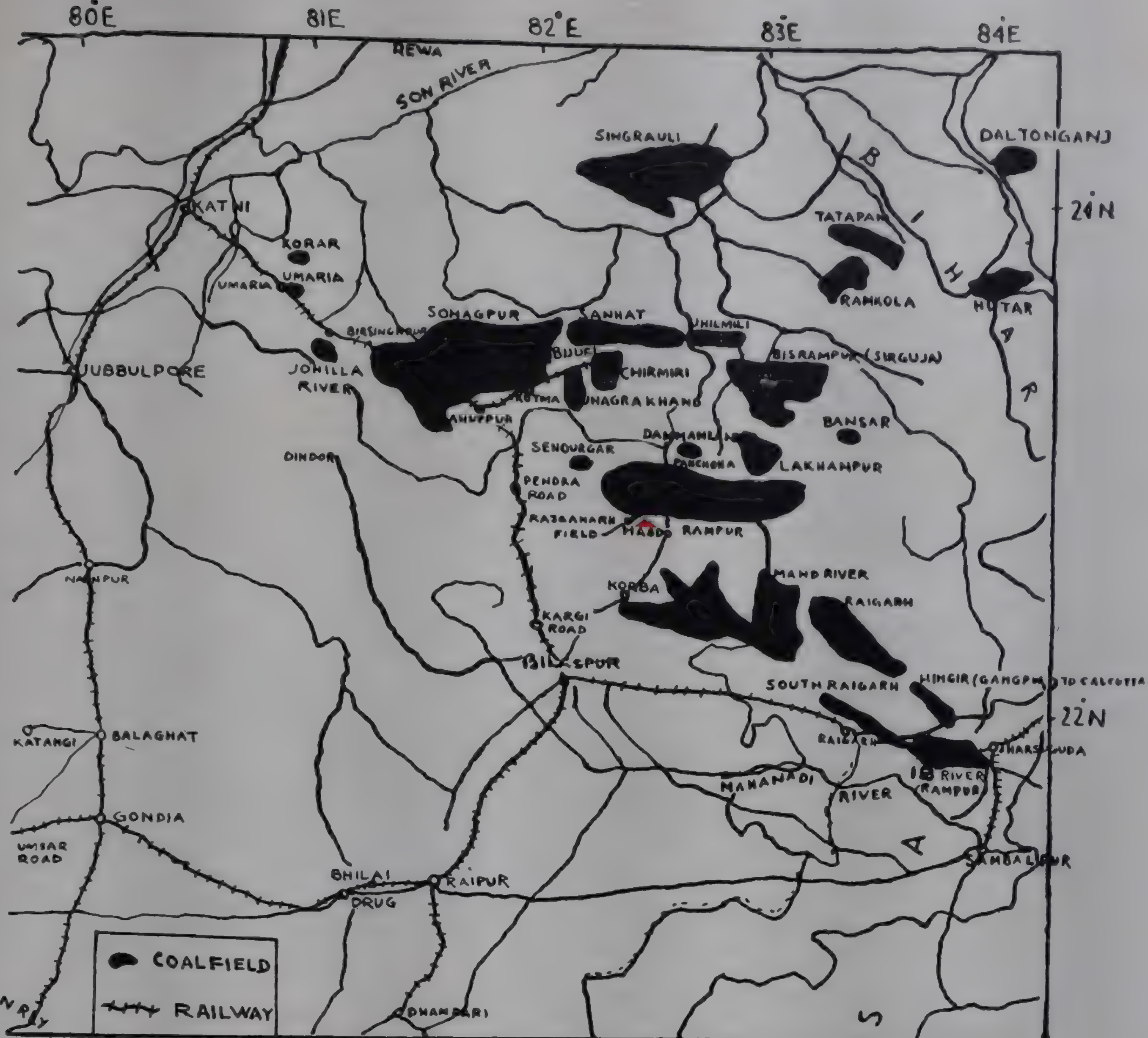

Fig. 1—Coalfields of Madhya Pradesh

The ash fusion temperature in mild reducing atmosphere showed an initial deformation varying from 1250° to 1450°C and the softening temperature is over 1450°C. Ash analysis indicated Fe_2O_3 content as fairly low (6 to 2.1 per cent). The Hardgrove Grindability index of this coal is of the order of 42 - 52. Its ultimate and low temperature carbonization analyses are as below (Tables 1 and 2).

TABLE 1—ULTIMATE ANALYSIS OF No. 2 SEAM (RAJGAMARH), %
(Air-dry basis)

Carbon	*Hydrogen*	*Sulphur*	*Nitrogen*
61.52-68.36	3.26-4.23	0.38-0.73	1.25-1.41

TABLE 2—LOW TEMPERATURE CARBONIZATION ASSAY OF No. 2 SEAM

Proximate Analysis (Dry Basis), %			*Yields/tonne of Dry Coal, Kg.*			
Ash	*V.M.*	*F.C.*	*Coke*	*Tar*	*Liq.*	*Ammonia*
12.2	33.9	50.9	755	105.6	52.1	96.0

The coal from No. 4 seam were tested with the idea of using them for steam-raising. Their moisture and ash contents (air-dry basis) are 3 to 5 and 27 to 36 per cent respectively, while Grindability index (H.G.I.) lies between 52 and 57. The proximate analysis and calorific values are given below:

Proximate Analysis, % (dry basis)			*Cal. Value, Btu/lb*	*Ash Fusion Temp., °C*	
Ash	*V.M.*	*F.C.*		*Initial Deformation*	*Softening*
34.7	25.9	39.4	14350-14870	1190-1450	1450

Fig. 2—Contour Plan of Rajgamarh Field Showing Different Grid Points

Notes & News

Fig. 1—A Bumper Paddy Crop at the Experimental Farm

Field Experimental Station at Sindri

The value of a fertilizer is decided ultimately by its behaviour under field conditions. For that matter, an industry-oriented fertilizers trials station has been established by the Planning and Development Division of FCI Ltd. at Sindri.The main objective of this station is to look into all problems relating to evaluation, utilization and demonstration of fertilizers produced by FCI and other manufacturers from all different angles, viz. rate of application, time and method of application, effect on the growth and development of various crops of economic importance, etc. As a matter of fact, the ultimate objective of this organization will be to attain an advisory self-sufficiency in matters of fertilizer field trials followed by their large-scale demonstration.

To translate this idea, a beginning has been made in March 1964 with only 25 acres of low-lying land with a view to expand this to 150 acres within a year or so. For most of the fabrication work, salvaged iron has been used.

Initially the land was rocky and highly undulated. Bulldozers were, therefore, employed for levelling and to bring the area into four distinct terraces, each having half-acre rectangular plots facilitating both irrigation and drainage. The dimensions of the plots have been so chosen as to fit in most of the experimental designs with various field crops.

All steps have been taken to mechanize and modernize the farm. Two Massey Ferguson tractors are operating with most of the improved implements like disc ploughs, harrows, tillers, graders, etc. Four 5 H.P. centrifugal pumps are used for irrigating the plots for general cultivation from a sewage canal running by the side of the farm, and also for experiments from a fresh water tank sunk inside the farm to avoid any complication from the heterogeneity of the sewage water. A glass-house has been constructed inside, and steps are being taken to make it fully temperature- and humidity-controlled so as to create an ideal environment for pot culture experiments under specific conditions. The construction of a field laboratory building, where all complex agronomical observations will be carried out, is complete. The primary preparation of plant and soil samples for chemical analysis will also be done in this laboratory. For day-to-day record of different environmental factors, such as temperature, humidity, rainfall, etc., a fully-equipped meteorological observatory has been established.

Another View of Paddy Crop Using Nitrophosphate

In this context, it would not be out of place to indicate here the results obtained from field trials in course of the past few months. Actually, the late *Kharif* season of the last year and the following full *Rabi* season have so far been utilized for cropping. During the *Kharif* season, two trials were conducted with *Aman* paddy (variety *Patnai*-23). A record yield, viz. 82.4 mds/acre of paddy, from one of the half-acre plots, has also been achieved with nitrophosphate fertilization. The attention of the Government has been brought to this. In the *Rabi* season, the worth of our fertilizers has been proved from the yield of brinjals. Although the harvest of this crop is not yet complete, the yield to date indicates a remarkably high figure. Some other experiments, such as on potatoes, have also been undertaken with a view to explore some new lines of research with fertilizer and on plant nutrition.

The present position calls on much of our time towards the basic development work, which in turn is necessary for the normal growth of research. But within a year we hope to accelerate our research work which might yield results useful to agriculture and thus help the Indian farmer.

Indian Chemical Society

Dr B. K. Dhar, Sarbasri N. B. Bhattacharyya and Dilip Kumar Mukherjee and Drs A. D. Pandey and V. S. Gupta attended the annual convention of the Indian Chemical Society held in the University of Allahabad, during December 26 to 29, 1964, under the chairmanship of Prof. R. C. Shah. The following papers from this Division were presented at the convention: (1) Behaviour of Different Fertilizers with some Typical Indian Soils: Part I—Physico-Chemical Properties of the Soils by S. C. Chatterjee, B. K. Dhar and B. K. Banerjee; (2) Behaviour of Different Fertilizers with Some Indian Soils: Part 2—Reaction with Phosphate Fertilizers by B. K. Dhar, S. C. Chatterjee and B. K. Banerjee; (3) Effect of Pressure on Catalytic Water Gas Shift Reaction by S. P. Sen, S. C. Aggarwal and K. R. Chakravorty; (4) Catalytic Conversion of Methane in Presence of Steam by S. P. Sen, N. B. Bhattacharyya, D. K. Mukherjee and K. R. Chakravorty.

In the first paper, S. C. Chatterjee et al have studied the role of all soil constituents, when different fertilizers are added to the soil. The efficiency of any fertilizer depends on the soil type and other microclimatic factors. The following representative soil samples were analysed and clay fractions in them identified by x-ray, DTA, and chemical methods: black soil at Amaravati, red clay soil at Sindri, IARI (New Delhi) alluvial soil, Jodhpur sandy soil, Ludhiana alkaline alluvial soil and Dinhata (W. Bengal) acid clay soil. Most of these soils have been found to contain illite and quartz with possibly small amounts of montmorillonite and kaolinite, except the black cotton soil which is rich in montmorillonite. The sharp basal line at 14-15 Å observed in most clays may be due to the presence of montmorillonite in the soil as an organo-clay complex. The base-exchange capacity and clay ratio (SiO_2/R_2O_3) are in agreement with other observations of identification. The soils are generally deficient in nutrient status, and base-exchange capacity is also low except in black cotton soils, where it is due to the predominance of montmorillonite in the soil clay.

In the Part 2 of the above paper, B. K. Dhar et al have studied the fixing power of some typical Indian soils mentioned above. Different soils gave different phosphate-fixing capacity. The duration of reaction seemed an important factor, and it takes at least 24 hr. to attain equilibrium for the fixation. The nature of clay minerals present in the soil have a distinct role in the phosphate fixation. Montmorillonite clays have less fixing capacity while illite types have high fixing capacity. When P_2O_5 is applied at the rate of 5 mg./100 g. of soil, there is complete fixation in soils, and that is the limiting dose.

In the paper on Catalytic Water Gas Shift Reaction, by S. P. Sen, S. C. Aggarwal and K. R. Chakravorty, the effect of pressure on conversion of carbon monoxide in presence of steam has been studied with three Fe_2O_3-Cr_2O_3 catalysts under various conditions of temperature, steam to gas ratio and space velocity. Application of pressure up to 12 atm. (abs.) increases the reaction rate, the effect being more pronounced when the reaction is shifted away from the equilibrium. Increase in concentration of steam up to a certain limit tends to increase the reaction rate. Experiments with two catalysts, having practically similar composition but differing in size, have indicated that at 1 atm. the lower size is more active. However, the accelerating effect of pressure is maximum with the bigger size catalyst and minimum with the lower. Catalysts having the same size and shape but differing in composition respond in a similar manner to pressure. Equal increments of pressure in different pressure regions do not accelerate the reaction rate to the same extent. In all cases the reaction rate falls beyond certain limiting space velocity, and with increasing pressure this limit is shifted towards higher space velocity region. The ratio of rate constant at particular pressure to that at 1 atm. has been found to vary between 4.633 to 1.213.

In the fourth paper presented at the convention by Sri D. K. Mukherjee, the authors have studied the reaction between steam and hydrocarbon fractions, comprising methane (60-70 per cent) and unsaturates (5-10 per cent) over five catalysts at 850°C fixing the pre-heater temperature at 600°C optimum. Three of the catalyst samples prepared in this laboratory are pure alumina-based, whereas the other two are imported and silica-alumina based. The results indicate the following: (i) catalysts irrespective of their methods of preparation show practically similar conversion efficiency at optimum reaction conditions; (ii) all the catalysts show increase in reaction rate with increasing steam to gas ratio up to 1.3 but increase beyond 1.5 causes considerable fall in their activity; (iii) of all the catalysts prepared the one from nickel carbonate showed maximum conversion of 92.7 per cent at 1.3 steam/gas ratio and at 380 S.V. Further increase in S.V. beyond 380 leads to decrease in conversion rate in all cases, the fall being minimum with the catalyst prepared from nickel hydroxide; (iv) presence of silica has no advantage over pure alumina in a carrier; and (v) even in the presence of unsaturated hydrocarbons in the feed gas none of the catalysts showed any marked carbon deposition. The authors have also discussed the kinetics of the reaction.

Among the other papers connected with fertilizers and soil chemistry presented at the convention, the following are worth mentioning: (a) 'Cation Exchange in Soil' by N. K. Banerjee and N. R. Dhar; (b) Evaluation of Ammonium Sulphate and Urea for Rice in Indian Soils' by J. Venkateswarlu and B. V. Subbiah, and (c) 'Mineral Content of Aquatic Foods' by R. Vishwanathan, F. N. Bhatt, C. Sreekumaran, B. R. Doshi, S. S. Gogate, A. N. Bhagwat and C. K. Unni.

In a popular lecture on Nitrogen Problem, Prof. N. R. Dhar dealt in brief with work being carried out in his laboratory at Allahabad on the fixation of nitrogen by organic matter. All types of organic compounds like glycerol, soluble carbohydrates, starch, celluloses, lignins, peat, lignite, bituminous coal, etc. undergo slow oxidation when mixed with oxides or phosphates of iron, aluminium, titanium, zinc or soil in moist condition and exposed to air both in sterile or unsterile conditions. The oxidation is markedly increased by exposing the system to light, and in this process of oxidation there is liberation of energy: $C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O + 676$ K. cal. This energy breaks up water molecules present in the system into hydrogen atoms and OH radical, and the atomic hydrogen so formed reacts on the molecular nitrogen present in the system and forms ammonia, while the OH radicals combine and form hydrogen peroxide which helps in the oxidation of organic matter. Their experiments have indicated that 50 mg. of nitrogen are fixed per gram of carbon in the organic matter oxidized in light and 25 mg. in the dark. When calcium phosphate is added, the nitrogen fixation may be doubled.

Effects of Urea & Ammonium and Potassium Salts

In soil, urea is hydrolysed to ammonium carbonate and the ammonium N is subsequently nitrified. The effects of solutions of urea and its decomposition products and their ammonium and potassium salts on the germination on the seeds of barley, wheat and kale have been studied at the Rothamsted Experimental Station, U.K. [Gasser, J.K.R., Chem. & Indus., No. 40, (1964), 1687]. Germination in these solutions was compared with that in distilled water using duplicate sets of 50 seeds on filter paper in a germinator kept at room temperature (18° - 20°C) and the germinated seeds were counted after 3 and again after 5 days. While the smallest concentrations of urea did not affect the germination of kale, these decreased the germination of barley and wheat. No kale or barley seeds germinated in the most concentrated solutions of urea but some wheat did. The solutions of ammonium carbonate and hydrogen carbonate decreased the germination of barley and wheat more than did the corresponding solutions of potassium carbonate and hydrogen carbonate. This increased damage can be attributed to the free ammonia in the ammonium solutions and not to the pH.

The effects of solutions of ammonium and potassium chlorides, nitrates and sulphates on the germination of barley are as follows: at the highest concentration, ammonium salts decreased germination more than corresponding potassium compounds. On average, chloride, nitrate and sulphate decreased the germination of barley; the effect with ammonium was greater than with potassium. The greatest concentration used decreased the germination of wheat, and again ammonium was more damaging than potassium. On average of all concentrations used, ammonium nitrate and chloride decreased the germination of barley more than potassium salts or ammonium and potassium sulphate.

Slow Acting High Analysis Fertilizer

Isobutyridene diurea (IBDU), a slow acting high analysis fertilizer developed by Mitsubishi Chemical Industries, has undergone successful field trials. They are constructing a 10,000 ton/yr capacity IBDU plant at Yokkaichi. A white crystalline powder, it is formed readily by a condensation reaction between urea and isobutyraldehyde, which is a by-product of Mitsubishi's 2-elthylhexanol plant. Its solubility in water is very low (0.1 - 0.19N/100 c.c.), but it hydrolyses very easily. The smaller the pH and higher the temperature of the solution, the more readily will IBDU hydrolyse. Thus, the most noticeable effects as a plant food may be expected when it is hydrolysed in a slightly acidic soil solution.

The 3-year agronomic tests have indicated that nitrogen in the form of isobutyridine diurea is sufficiently slow-acting when blended with granular NPK mixed

fertilizer of appropriate composition and particle size, and several grades of the mixed fertilizer are going to be produced. The rate of release of available nitrogen from IBDU-containing mixed fertilizer depends on the rate of dissolution of the substance in soil solution, and can be controlled by adjusting the size as well as the hardness of the granules. For vegetable crops and fruit trees, the following mixed fertilizers are used: 15-15-15, 1B-N8; 18-11-11, 1B-N6; 16-10-14, 1B-N8.

[Nitrogen, 31, 1964, 34]

New Ammonia Synthesis Design

The recent considerable increase in the consumption of nitrogenous fertilizers have aroused interest in very large ammonia units. Some of the projects under study now call for a capacity of 1000 tonnes of ammonia per day or even higher. Recent introduction of centrifugal compressors has made it desirable to design for a pressure range in the order of 150 atm instead of 250-400 atm often used at present. The lower pressure favours the design of large inner diameters of vessels. The possibilities of modifying the classical converter designs —such as the TVA and quench types— in such a way as to make possible the use of pressure shells without full diameter closures has been considered. This would call for some assembly inside the pressure vessel and would involve problems with respect to cooling of the high pressure shell and complications of the catalyst charging and emptying procedures.

Using radial flow technique it is possible to design for capacities about 1000 tons/day and with present fabrication facilities 2000 tpd units are within the realm of possibility. In the radial type, the flow through the catalyst bed (one bed or several beds) is from a central pipe towards the wall or from an annulus around the catalyst bed towards a central pipe. Pressure drop in this converter is extremely low, even when using catalyst of a small particle size and using considerably higher space velocities. The basket is extremely simple and can be insulated on the outside. The converter can be designed for flow of the cold in-coming gas down through the an annulus between the basket and the pressure shell. In some cases, it may be desirable to have catalyst section and heat exchanger in separate pressure shells. A typical radial flow 1000 tpd ammonia converter would have the following dimensions: inner diameter of pressure shell 2.28 m. inner height of pressure shell 17m, catalyst volume 37.10m^3. At 150 atm. operating pressure, 12 per cent inerts, 2 per cent ammonia at inlet and a space velocity of 16,500 V/V/h, this converter would give 1000 tpd production with a 3-year old catalyst.

Improvements in catalysts, such as the use of promoted iron oxide catalysts, have led the designers to move towards the same operating pressure range and most plants built recently have ranged between 250 and 400 atm and fall into the following two groups: in one the heat of reaction is removed by heat exchange in the catalyst bed; in the other this heat is removed by splitting up the catalyst section into a number of beds and cooling the gas between the beds either by means of cold or by quench with cold gas. In all designs the flow of gas is either downwards or upwards through the catalyst bed, and in large units space velocities are limited. Pressure drop considerations would make it desirable to use even larger particles involving larger catalyst volumes. Illustrating a TVA-type 5000 tpd ammonia converter, useful data have been cited to demonstrate how the size of the synthesis gas converter is effected by the method of manufacturing the gas.

The recent trend in the manufacture of synthesis gas is towards the following sequence: high gas pressure reforming, low temperature shift conversion, CO_2-removal and methanation. The resulting make-up gas contains about 1 per cent inerts, and the operating economy normally requires that in the order of 12 per cent inerts must be tolerated at converter inlet. Increasing the inerts from 2 to about 12 per cent will normally make it desirable to increase both circulation rate and catalyst volume. Assuming an increase of the circulation rate in the order of 10 per cent, the catalyst volume will have to be increased by some 35 per cent, which means that a 5000 tpd unit calls for a converter pressure shell with an inner diameter of 56 inches.

It is clear that without deviating from normal design practice, which over the past few years has proved to be economically optimum, design of the very large units, such as with capacities 1000 tpd and higher, presents mechanical problems, which in turn get very much accentuated when adopting lower pressures and a synthesis gas with high inert level. To permit the construction of larger units, some new concepts, such as provision of synthesis loops, can be investigated.

[Nitrogen, 31, (1964), 22-27]

Agricultural Conditions & Choice of Fertilizers

Most tropical soils are deficient in phosphate. As agriculture becomes more highly developed with use of fertilizer, usefu reserves of nutrients like phosphorus and potassium accumulate in the soil, while nitrogen reserves are depleted by continuous cultivation. Since inorganic nitrogen is easily lost by leaching and denitrification processes, little reserve of nitrogen accumulates in soil under arable farming systems. Nitrogen applied is now more heavy than phosphorus. Recent field experiments in Europe show that non-legumes give much higher responses to 1 Kg of N than to 1 Kg. P_2O_2 or K_2O.

For developing very poor soils for cultivation, the first need will be for phosphate, which is also important for stimulating rapidly-growing food crops on many kinds of soil and for maintaining the phosphate level of improved soils. Potash is required after intensified farming has been established; its greatest need is on highly leached soils, particularly for commercial crops. Where fertilizer use is beginning, it is important to try to get maximum returns from the moderate dressings, so that the crop takes up maximum quantities and minimize fixation by soil. When farming is more highly developed, efficient fertilizer use will involve determining how best to use nitrogen to control the level of production and finding how much P and K must be used. Whenever new methods of cultivation becomes possible, field tests may have to be done, but in choosing fertilizers for use in experiments advantage should be taken of experience gained elsewhere. In dry regions fertilizers may be unprofitable, but they are likely to become essential for high yields if irrigation becomes possible.

Among nitrogenous fertilizers, anhydrous ammonia is the most concentrated nitrogen fertilizer. It has to be placed at least 15 cm below the soil surface to avoid loss, but the special equipment needed for its transport and application make it costly. Aqueous ammonia (21 - 29 per cent N), made by dissolving ammonia in water, is easier for farmers to handle, but it has also to be placed below the soil surface. Nitrogen solutions, usually containing less than 30 per cent N, are made from ammonium nitrate urea and ammonia. These are easier to handle than anhydrous ammonia.

Liquid nitrogen fertilizers are becoming important in USA and some other countries, their main advantage being their low cost. These require to be injected into the soil before planting or to be applied as side-dressings to established row crops; only 'non-pressure' solutions are suitable for applying on the soil surface but if they contain free ammonia they may scorch the foliage. But liquid fertilizers are unsuitable for application by small farmers; such fertilizers containing P and K as well as N are however now being sold.

All nitrates behave similarly; they are unsuitable for water-logged soil, particularly for wet rice-growing.

In soil, urea (46 per cent N) is rapidly converted by enzyme action to ammonium bicarbonate, which is unstable. If this change occurs on or near the soil surface, ammonia may be lost to the air. It has storage problems.

Ammonia gas may be lost, when ammonium salts are used on soils with pH above 7, the effect is more serious with light soils having low cation-exchange capacities. Losses may occur from all fertilizers that give free ammonia in the soil; losses from ammonium sulphate may be quite high on calcareous soils.

From nitrates, the best known example of loss of nitrogen is when they are used for wet rice, for which ammonium sulphate is more efficient than potassium and sodium nitrates. Denitrification, which is not known in tropical agriculture, may cause serious losses of N in 'dry-land' cultivation in temperate region. Leaching of nitrate always occurs where drainage water passes down the soil profile. It should be estimated, when planning the methods of its application and choosing the forms of N. Leaching losses are most severe from light soils with poor structure.

But use is made of nitrogenous fertilizers when they are matched to soil and crop. Ammonium salts and urea should not be used for top dressing on light alkaline soils; nitrates are better. Urea seems satisfactory for wet rice growing; nitrates should not be used on water-logged soils or when irrigation water may wash them into the drains. Leaching losses at the end of the growing season are difficult to prevent, but during the season they may be minimised by repeated small dressing of nitrogen carefully timed to avoid having much more surplus nitrate in the soil at one time. Ammonium salts are held by clay soils and are not leached, but they are nitrified at quite low temperatures, and very rapidly in warm soil, so loss of nitrate by leaching is not prevented by using ammonium forms. It is possible to inhibit temporarily the microbiological transformation of ammonium to nitrate by adding a small amount of 2-chloro-6-trichloromethyl pyridine to the fertilizer. Future progress may come from using insoluble compounds of nitrogen, such as urea condensed with formaldehyde, yielding nitrate slowly in the soil. TVA has tested oxamide, a sparingly soluble fertilizer and at present expensive, and results have indicated that it must be decomposed microbiologically before crops can use the nitrogen; its rate of action can be controlled by varying granule size, surface area governed the amount dissolved in unit time. Experiments in temperate countries have indicated that only 30-50 per cent of nitrogen dressing is recovered by arable crops and perhaps much of the remainder is lost.

The common forms of phosphates used as fertilizer can be divided by their solubility as follows: (1) water-soluble, (2) (2) slightly-soluble and (3) almost insoluble.

(1) *Water-soluble Phosphates:* The differences in the effects on crops of mono-calcium phosphate (superphosphate and triple super-phosphate) and mono-and di-ammonium phosphates are caused by differences in their co-ions.

(2) *Slightly-Soluble Phosphates*: Dicalcium phosphate is the only important fertilizer now in this group. It is mostly used as a component of compound fertilizers made by ammoniating superphosphate or triple super, or by nitrophosphate processes. Dimagnesium and ammonium magnesium phosphates may become important in future.

(3) *Almost Insoluble:* This group includes rock phosphates, basic slags and phosphates made by high temperature processes. These range from iron and aluminium phosphate to compounds that are less soluble than fluorapatite. Rock posphates are cheap, but are only effective on acid soils and should be ground; slow-acting and may not be suitable for quickly-growing crops, these should be mixed with soil to have maximum effect, and recent work in Australia has shown that they act more quickly when they are granulated with sulphur. A complete valuation involves measuring immediate effects and residual ' alues.

Heat treated phosphates are similar to high quality basic slags and are intermediate in value between rock phosphates and fertilizers containing dicalcium phos phate. Most effective on acid soils, they are difficult to mix with other fertilizers and their making is justified where fuel and power are cheap and sulphuric or nitric acids are expensive.

Basic slag, a useful by-product from steel-making, is satisfactory provided most of its phosphorus is soluble in standard tests using 1 per cent citric acid solutions. Magnesium and manganese in it are also useful.

The few water-soluble potassium salts, used as fertilizers, are water-soluble, and the potassium ions in them have the same effects on crops, but different fertilizers, because of the different anions accompanying the potassium, have different overall effects on soil fertility and leaching from soil. A leachability scale established by Munson and Nelson is: $KCl > KNO_3 > K_2SO_4 > KH_2PO_4 > K_2HPO_4 > KPO_3$ $K_2C_aP_2O_7 > K_2CO_3$. In many tropical soils, poor in base, there is no mechanism for fixation and release of K, in which extra leaching causes serious loss of catious.

[Cooke, G. W., Paper Presented at the ECAFE Conf. on the Development of Fertilizer Industry in Asia & Far East, held in Bombay, Nov. 18-Dec. 2, 1963]

Research on Oil Gasification in India

By 1966 the total refining capacity of the Indian oil refineries is expected to reach 17 million tons. The pattern of consumption of the petroleum products indicate that there is a rising demand of middle distillates and fuel oil, which may even be more than the envisaged production, but the demand of motor gasoline is quite low so that considerable quantity of this product will remain surplus. It becomes therefore important to gainfully utilize the surplus naphtha for producing gases—fuel, synthesis and olefines—fertilizers and petrochemicals. In fact quite a few such industries have been planned to use naphtha.

Research work has been undertaken at the Indian Institute of Petroleum, Dehra Dun, on the steam-cracking of naphtha with the idea of developing economic processes under Indian conditions for production of (1) hydrogen or hydrogen-rich gas and (2) town gas. The feeds of both are straight-run naphtha cuts from Indian crudes; some of these do not need any pretreatment before being subjected to the reforming operations.

Using a catalyst prepared mostly from cheap indigenous materials, conditions have been developed in bench-scale experiments to get about 90 per cent conversion of naphtha to a hydrogen-rich gas. Efforts are being made to extend the period of continuous reforming without regeneration by slight variations in reaction parameters. Simultaneously, designing work is going on for scaling up production to 15 Nm^3/day of pure hydrogen.

Work on the laboratory scale town-gas unit is also progressing; conversions over 90 per cent are readily obtained, though the maximum calorific value as yet realized for the product gas is only 3200 Kcal/Nm^3. The optimum required value is 4200 Kcal/Nm^3. Efforts are being made to improve the C.V. without post-reforming enrichment by varying reaction conditions on a few of the several catalyst specimens already investigated. The design of a pilot plant to provide about 500 Nm^3/day of gas to the Institute and its colony will soon follow.

[Communc. from I.I.P., Dehra Dun]

Fertilizer Industry in Middle East

A £4m. nitrogenous fertilizer plant is being planned by the Lourho Organization at Untali, Rhodesia. A contract for the design, construction and start-up supervision of a complex nitrogenous fertilizer complex at Gabes, in Tunisia, has been awarded to Cia Tecnica Industria Petroli SpA. The £30 m. complex for Industries Chimiques Maghrebines will have a 65,000 ton/yr anhydrous ammonia plant and facilities for 200,000 tons/yr. ammonium phosphate and 80,000 tons/yr ammonium nitrate, most of which will be exported.

Iraq is planning for a £ 27.8m. plant for daily production of 200 tons ammonium nitrate, 150 tons urea, 300 tons sulphuric acid and 400 tons of ammonium sulphate at Al Bassrah for which the Japanese Consulting Institute has provided technical advice. Esso Fertilizer Co. SAL, in combination with local business interests, will build a fertilizer plant of 130,000 tons/yr total capacity at Ras Salaata, about 35 miles north of Beirut (Lebanon), which will have facilities for manufacturing nitric acid, ammonium sulphate, nitrogen solutions, calnitro and complex fertilizer.

Kuwait Chemical Fertilizer Co. will build a 400 ton/day ammonia, a 550 ton/day urea, a 400 ton/day sulphuric acid and a 500 ton/day ammonium sulphate plants at Shuaibah.

Occidental Petroleum has negotiated with the Saudi Arabian Government for construction, operation and sale of output from an ammonia plant to be built. Natural gas will be furnished at the well-head without cost until 1984 and Occidental's subsidiary, International Ore and Fertilizer Corpr., will market the output.

[Chemical Age of India, 16 (1965), 2, 174-175]

Nitrogen Fertilizers in China

China had embarked on her 5-yr plan in 1958, and after finding discrepancies between raw material and processing industries in the first two years, the Government stipulated a readjustment policy in 1961, which envisaged almost a 30 per cent increase in agricultural production by 1969. It was proposed to expand the cultivated area fourfold to 145 million hectares with a simultaneous expansion of chemical fertilizers production to over 15 million tonnes by 1969 from 2.48 millions in 1960.

Chinese soils are estimated to be 80 per cent nitrogen-deficient and 50 per cent deficient in phosphates. Approximately two-thirds of the total production originates from large chemical complexes such as those as Kirin, Nanking, Dairen and Taiyuan, and more recently Wuching and Canton.

Kirin plant, built with Soviet aid, came on stream in 1955 with a capacity of 75,000 tpa of ammonia from gasification of low-grade coal. Granular ammonium nitrate was the product. Nanking plant, dating back to 1934, was the first Chinese chemical fertilizer unit which was rebuilt after the second World War. Now one of the largest chemical complexes, it is capable of producing 50,000 tpa of ammonia, based on anthracite, 195000 tpa ammonium sulphate, 200,000 tpa, sulphuric acid, 400,000 tpa superphosphate and 10,000 tpa potassium sulphate.

Dairen plant, reconstructed in 1950, has resumed production in 1953. It has now an estimated capacity of 25,000 tpa of ammonia used principally to make ammonium nitrate.

Commencing production of nitrogenous fertilizers by the end of 1960, the Taiyuan plant is believed to have expanded substantially from an initial capacity of 25,000 tpa.

Among the new installations which have recently been completed, Wuching chemical works at Shanghai was commissioned in September 1963 with a capacity of 25,000 tpa NH_3 to manufacture 100,000 tpa of ammonium sulphate. A similar size plant has gone into full production in early 1964. The new chemical plant at Kaifeng, in Honen province, is reported to have commenced production of synthetic ammonia and ammonium sulphate in March 1964. A new electric-powered ammonium magnesium phosphate plant, capable of producing 7,300 tpa, was opened in Canton in May 1964, and other plants are under construction at Hengyang and Tsinau. Then there are several small synthetic ammonia plants, each producing 800-2000 tpa NH_3.

In the Chinese production pattern, ammonium sulphate and ammonium nitrate predominate but recently priority has been given to ammonium nitrate. Ammonium bicarbonate and ammonium chloride are also produced to the extent they are available from the soda ash plants, and there are also two medium scale calcium cyanamide plants in operation at Kirin and Kiangsi.

The major producer of ammonium chloride is the Tsingtao complex having an estimated output of 700,000 tpa. Tienstsin has a 190,000 tpa ammonium chloride plant using Hou process. Another producer is Kwangchow, producing in addition ammonium sulphate, has a production capacity of 50,000 tpa NH_3.

There is a trend towards the introduction of higher-concentration fertilizers and the first ammonium phosphate plant is under erection. Special attention has been paid to urea and a new 40,000 tpa plant is being added to the Wuching complex. China has purchased a £ 2-3 million urea plant of 500 tpd capacity from Netherlands, using Stamicarbon process, which will be located near Luchow. Other recent agreements include the purchase of 2 ammonium nitrate plants—each having a capacity of 100,000 tpa—from Montecatini at £ 7.2 million. A special fertilizer design department in Shanghai is now designing its fourth fertilizer plant, which will have a capacity of 100,000 tpa of nitrogenous fertilizers, and according to reports another six fertilizer plants are to be installed, along the lines as that as Wuching, in Anhwei, Honan & Hopei provinces. China National Technical Import Corporation is negotiating with Daiichi Tsusho & Toyo Engineering for the purchase of an American £ 5 million

urea plant of 180,000 tpa capacity.

[Nitrogen, No. 31, (1964), 14-17]

Nitrogenous Industry in Yugoslavia

Wider application of fertilizers for the expanding agricultural production has been the basis for the acceleration of development of fertilizer and other sectors of industry. Considerable investment resources have been diverted to the expansion and modernization of plant capacity. There is substantial boom in demand of nitrogenous fertilizers, in which self-sufficiency is likely to be attained by 1966.

Although the production of superphosphates has continued to dominate, a major expansion in nitrogenous fertilizers production has been brought about due to the availability of raw materials for sulphuric acid and of sources of natural gas. Although demand is increasing rapidly, the commissioning in 1962 of two large nitrogenous fertilizer complexes at Pancevo and Lukavac and the calcium cynamide plant at Jegunovci has served to reduce Yugoslavia's dependence on imported materials. In addition, two new plants—at Kutina and Velenje—are under construction, which when completed will transform that country into a net exporter. In 1958 the nitrogen capacity was at 38,500 tonnes, which was taken up by two calcium cynamide plants —at Ruse and at Dugi Rat—and there was by-product ammonium sulphate from Lukavac coal coking plant. In addition, the synthetic ammonia plant at Gorazde manufactured ammonium nitrate. The nitrogen capacity has increased nearly fourfold to its present level of 138,000 tonnes N. The large complex at Panveco, which went into production in November 1962, has an annual output of 360,000 tonnes of lime ammonium nitrate (N 20.5 per cent). Earlier in 1962, the 8.5 million Boric Kidric chemical works at Lukavac, based on high caloric coke oven gas having a capacity of 370 tpd of lime ammonium nitrage and constructed by Montecatini and Ansaldo of Italy, went into operation.

The new plant at Kutina based on refinery waste gases from a nearby refinery at Sisak, when completed in 1966, will have a capacity of 800,000 tonnes of nitrogen fertilizer. The complex at Velenje which is at present in the preparation stage, when completed will use about 2 m. tonnes of lignite each year, which will be dried and carbonised and the gas to be used to manufacture 33,000 and 46,000 tonnes of ammonia and urea.

The recent expansion in production facilities has been undertaken for a 2 m. tonnes target for total fertilizer output by 1965, and by 1963 the output is estimated to have reached a level of 70,000 tonnes of N, representing a 100 per cent increase over the previous year. The consumption pattern has been dominated by ammonium nitrates, esp. lime ammonium nitrate, but urea has not yet made any impact. In a few years, Yugoslavia will be in a position to develop a significant export trade in nitrogenous fertilizers with the Middle East, Greece & North African countries.

[Nitrogen, No. 30, (1964), 18-22]

Indian Current Science Abstracts

The Indian National Scientific Documentation Centre (INSDOC) has decided to publish a new bibliographical periodical from early this year entitled Indian Current Science Abstracts. This has replaced the Bibliography of Scientific Publications of South and South-East Asia. As far as possible, efforts will be made to include scientific communications published abroad by Indian nationals. Original articles, short communications, critical reviews and informative articles published in scientific and technical journals or in proceedings of scientific conferences, symposia, etc. monographs and other *ad hoc* publications, as well as patents and standards, will be noticed in this publication. The annual subscription for this publication will be Rs. 50.00 only.

The INSDOC has appealed for proper cooperation from all concerned for sending copies of all scientific publications, reports, monographs including reparints of papers published in foreign periodicals to the following: Indian Current Scientce Abstracts, Indian National Scientific Documentation Centre, Hill Side Road, Delhi 12.

News in Brief

Gasification of Liquid Hydrocarbons

In the annual general meeting of the Institution of Gas Engineers in June 1964, Prof. C. Padovani, Director, Stazione Sperimentale per i Combustibili, Milan, gave a review of processes for the gasification of liquid hydrocarbons and of researches carried out in his laboratories.

Oil gasification processes based on pyrolysis are considered and also these on oxygenolysis and hydrogenolysis, and continued catalytic autothermic oil gasification with steam under pressure. In the experimental station at Milan, attention is now being devoted to techniques and processes for the direct gasification of crude oils as it is thought conditions could arise to make such a raw material economic or interesting for producing gas. Two general methods are being considered.

The first one is a development of Padovani's hydrogenation techniques, in which the crude petroleum is submitted to de-asphalting, de-ashing and partial de-sulphurizing operations before hydro-sulphurization and hydrogenation. The second method includes a preliminary splitting of crude oil into a residue and a distillate. The two fractions are afterwards submitted to separate gasifying processes.

[Fuel, 43 (1964), 399-400]

Needs of Tropical Soils

In the whole great area of the tropics, less than 2 million tons of plant nutrients (nitrogen, phosphorus and potassium) are used, most of them on plantation crops, whereas over 26 million tons are used in temperate climate countries. Thus the use of fertilizers in the tropics has hardly begun, and a great expansion in the present use is expected which will help in supplying food for the rapidly expanding population in the tropics.

Small responses are obtained to fertilizers where the rates of application are very low as used on peasant-grown crops. But as experience increases and the fertilizer/crop price ratio improves, heavier rates of application will be made and greater responses obtained. Even under present circumstances, average responses of 25 to 75 per cent increase are common in tropics. Instances of doubling the yield are also not uncommon.

The improvement of cultural practices usually coincides with an improved response to fertilizers. This does not, however, mean that fertilizers should not be introduced to primitive farmers until they have adopted better varieties and cultural methods. Excellent results have been and are being obtained using fertilizers even without other improvements.

The fertilizer needs of the tropical crops are closely linked with rainfall zones and with the textural soil classes in which they are mainly grown as well as with their own physiological requirements. Nitrogen is the most generally needed and effective of the primary nutrients in the tropics. Phosphate is also very widely needed; on the average, it gives smaller responses than nitrogen, yet when it is acutely deficient, phosphate replaces nitrogen in first importance. In such circumstances, nitrogen and phosphate together can be very effective. Potash is generally less needed. But as the use of nitrogen and phosphate increases and as crop production levels rise, potash will doubtless become more widely necessary.

[Richardson, H. L., Internat. Sugar J., 66 (1964), 775, 141; Abstr. FAI Abstr. Ser. 3 (1964), 7, 2-3]

Single Stage Fertilizer Process

A process, developed by a Scottish firm, reduces to a single stage the production of fertilizers in hard dry, spherical granules of uniform size. Each granule, a complete and balanced plant food in itself, is built up layer upon layer rather like onion skins in two drums revolving one inside the other in which sulphuric, nitric and phosphoric acids are reacted with ammonia to give a dry granular product. The chemical energy liberated as heat during the process is used to evaporate all the water present.

The two acids and the ammonia, together with crystalline potash form an existing store, are accurately fed in the correct proportions, according to the analysis of the end-product, into the two concentrically rotating granulating drums. As they pass round the cycle, the particles are coated in turn by a layer of phosphoric and nitric acids, these being immediately neutralised by ammonia. Potash salts are also included during the cycle so that each layer contains all three plant foods in the correct ratio. The granules are coated with a specially developed non-toxic non-corrosive powder to ensure free-flowing properties. This fertilizer is available in two forms, viz. one with a high potash content and the other with a high nitrogen content.

[Chem. Tr. J., 154 (1964), 4016, 774; Abstr. Res. & Indus., 9 (1964), 238]

Ammonia as a Fuel

Ammonia has been used successfully as a fuel in a 1.5 hp, internal combustion military engine for 35 hr without a break-down, and research workers at the U.S. Army Material Commands Engineering Research & Development Laboratory found that a 4 : 1 ratio (by volume) of NH_3 to H_2 when burnt with air would start the engine and operate it at 3,300 rpm with about 80 per cent of the power of gasoline.

[Chem. & Engineering News, 42 (1964), 39, 54]

ICI Uses Japanese Urea Process

In the Billingham (U.K.) plant, ICI will be using Toya Koatsu's total recycle urea process. This 1,000 tpd urea plant, costing about £ 5 to £ 6 million, will come on stream at the beginning of 1966. The advantages claimed are a high quality product as a free flowing prills, mild operating conditions, simple reactor design and operation and high conversion giving smaller equipment.

[Chem. Age, 92 (1964), 2362, 595]

Gas Council's Town Gas Process

The details of the first gas plant to utilize the U.K. Gas Council's catalytic

rich gas (C.R.G.) process for the production of town gas directly from light distillate are now known. The plant for the Eastern Gas Board at Hitchin produces 30 mcfd of town gas in a Series A design, incorporating the C.R.G. process for the production of rich gas, which is then fed to a tubular reformer—in this case a Selas design—which converts part of the output to lean gas. The two outputs are mixed to produce town gas of the required quality. Facilities included in the plant are for desulphurazation of the feed stock, CO_2 removal, CO conversion, steam generation, water treatment, etc.

The largest gas plant using this process that is being built at Killingholme for the East Midlands Gas Board by Woodall-Duckham will produce approximately 60 mcfd of enriched gas.

[Chem. Age, 92 (1964), 2362, 595]

Cyanuric Acid for Promoting Nitrogen Fertilizer Effects

Onodo Chemical Industry Co. of Japan has released the results of its investigations on the use of cyanuric acid and derivatives as slow-acting fertilizers. Pot experiments using this acid and its derivatives, like cyanuric chloride and triisourea, have been carried out. Triisocyanuric acid is found to be the most effective retarder when more than 3 per cent is applied. Potassium diisocyanurate was also satisfactory in quantities over 3 per cent. Full-scale farm trials are now being implemented.

[Nitrogen, No. 31, (1964), 37]

Glass Phosphate Fertilizer

Several insoluble phosphorus compounds have been made soluble by silica, and on mixing them a new glass fertilizer has been obtained by a Russian chemist. Unworkable low grade phosphorites are poured with phosphoric acid in a gas furnace, the solution is evaporated and the residue dried and melted. The melt is tapped from the furnace, and upon solidification it is crushed. This glass fertilizer, produced at the cost of double superphosphate, on field testing at the Potato Institute and other research establishments has yielded very good results.

[Chem. Tr. J. & Chem. Engr., 156 (1964), 417]

Some Patents

(*I*) *Urea Syntheses, Stamicarbon N. V. Br. Pat.* 952, 764: The urea melt produced from NH_3 and CO_2 and containing ammonium carbonate is stripped therefrom with CO_2 at a pressure of about 10 atm. The ammonium carbonate, expelled as NH_3 and CO_2, together with the CO_2 used for stripping are used for the urea synthesis. Part of the total CO_2 may be reacted with NH_3 and the remainder of the CO_2 is used in the stripping, condensed with the stripped gas and returned to the reactor as carbonate solution or suspension, or alternatively the gas mixture from the stripping treatment may be fed directly to the reactor.

[Chem. Tr. J. & Chem. Engr., 155 (1964), 427]

(*II*) *Purification of Methanol; Chem. Construction Corpr. Br. Pat.* 958, 828: Crude synthetic methanol is purified from high and low boiling impurities by extractive distillation with water to produce a bottom stream of aqueous methanol, followed by the fractional distillation. The extractive distillation stage being characterized by the removal of a liquid side stream comprising high boiling impurities and some methanol from the middle section of the column, the extraction of this side stream with water to remove a portion of the high boiling impurities as a water-immiscible phase back into the middle section of the column.

[ibid]

Panveco Fertilizer Complex

One of the world's most modern complexes has gone in operation near Belgrade using natural gas piped from the eastern part of Yugoslavia. Designed by Chemical Construction Corporation of U.S.A., the gas is converted into synthesis gas using the Texaco partial oxidation process and with nitrogen formed into ammonia using the Chemico-NEC process. The anhydrous ammonia formed is converted first to nitric acid and then to ammonium nitrate (33.3-35 per cent N), some of which is mixed with limestone. Chemico processes are also used for the manufacture of nitric acid and for neutralization under pressure of nitric acid with ammonia. The Panveco plant can also utilize crude oil in place of natural gas. In order to ensure continuity of operation the complex has two oxygen plant, three Texaco gas generators (two for natural gas and one for crude), two CO-conversion units, two water scrubbers for CO_2 removal, two nitrogen wash units, two nitric acid plants and two installations for manufacture of ammonium nitrate and nitrochalk.

The ammonia plant, designed for production of 300 tpd ammonia in two trains, is based on nitrogen produced in an air separation unit, and hydrogen is produced by the Texaco partial oxidation process. The nitric acid plant produced 56 per cent nitric acid.

[Nitrogen, 1964, 30, 23-29]

Fertilizer Developments in UAR

The UAR Government and the Egyptian Organization for Industrializations have signed a $ 7.0 m. contract with BASF and Uhde of Germany to undertake the supply and installations of plant for a large extension to the Suez fertilizer complex. Ammonia capacity has to be increased by 125,000 tpa, and production of calcium nitrate and CAN will increase to about 275,000 and 165,000 tpa against the present productions of 260,000 and 100,000 tpa respectively. A 170,000 tpa nitric acid plant using Stamicarbon process is to be built at Helwan by Continental Engineering NV of Holland.

Chemical for Agricultural Development

A versatile chemical product, named Cycocel, has been developed in the laboratories of Michigan State University, U.S.A., which is expected to have far-reaching effect on agriculture under unfavourable conditions. A derivative of chloroethyl-methyl ammonium chloride cycocel would make it possible to cultivate crops in countries subject to unpredicatable drought conditions. Cycocel treated plants grow shorter, sturdier, more resistant to wilting and require less water. An yield of wheat higher by as much as 50 per cent has been obtained in test plots.

[Res. & Indus., 9 (1964), 307]

Drying of Ammonium Sulphate

A process has been developed in U.S.S.R. for drying ammonium sulphate as it moves along a curved path by preheated air or fuel gas blown in at a tangent through jets inside the eddy chamber. The apparatus ensures a close contact between the material and the heat carrier, a high throughput and efficient drying of the product.

[NPKS Abstr., 35 (1964), Nov., 5]

Protein from Petroleum

The work first started by a French research team of the Société Francaise

des Petroles BP refinery at Lavera on the action of a great variety of micro-organisms on hydrocarbons has led to the development of a process of manufacture of protein. Under suitable conditions, a certain number of micro-organisms selectively metabolize the n-paraffinic hydrocarbons of petroleum fractions, leaving the other almost untouched, and by selecting suitable culture conditions, the growth of these micro-organisms on petroleum fractions is as fast as on conventional sugar media. For studying petroleum fermentation, a semi-commercial plant has been set up comprising the following sections: fermentation, harvesting of micro-organisms with recovery of unmetabolized gas oil and the purifying and drying of micro-organisms. Consideration is now being given to the establishment of pilot-scale animal feeding trials under tropical conditions in Nigeria.

[Champagnat, A., Chemical Age of India, 16 (1965), 2, 110-115]

Slow-Release Fertilizer for Cotton

A new slow-release nitrogenous fertilizer—described as a combination of urea and formaldehyde—has been produced by the Chirchik Electrochemical Works in Uzbekistan (U.S.S.R.). This fertilizer has proved very effective on cotton and has resulted in increased yields by over $2\frac{1}{2}$ cwt per acre compared with controlled plots.

[Nitrogen, Na30, (1964), 35]

Production of Nitrogen

World production of nitrogen fertilizers rose by 12 per cent in 1963-64. It is estimated to have totalled 15.2 million tons. Nearly one-quarter of the increased output was achieved in developing countries of Europe, Asia, Africa and South America, just over one-fourth in the U.S.S.R. and Eastern Europe and the balance—about one-half—in the western countries.

[FDC Israel News-Letter 4 (1964), 12,7]

New ICI Fertilizer

The new fertilizer—Nitram—which is prilled ammonium nitrate with a much higher concentration than usual of available nitrogen (34.5 per cent) has been introduced by the Agricultural Division of I.C.I. to provide the farmer with a dressing that can be applied at a much lower cost than previously. It cuts storage costs by 40 per cent and is packed in heavy grade polythene sacks. Much research work was needed to develop a blending agent that would prevent the compound from absorbing water very rapidly from atmosphere.

[Chem. Age, 92 (1964), 2370, 901]

Miscellancous

Sri M. Mazumdar, M. Sc., Asst Technologist, P & D Division FCI Ltd., has been elected an Associated Member of the Institute of Fuel, U.K.

PRICES OF NITROGENOUS FERTILIZERS

Type of Fertilizers	*Cost per Tonne, Rs.*	*Pool Issue price per Tonne, Rs.*	*When sold for the use of tea, coffee or rubber plantations, Rs/tonne*	*Consumer Prices Per Tonne (Rs.)* when sold for the use of Cultivators*			
				In Uttar Pradesh	*In Madras*	*In Orissa*	*In any other State or Union Territory*
Ammonium Sulphate ..	332.27	330.00	374.60	366.00	370.20	373.00	360.00
Urea ..	478.09	570.00	615.00	615.90	617.40	615.00	615.00
Calcium Ammonium Nitrate ..	295.00	278.00	310.00	314.00	319.60	321.00	310.00
Ammonium Sulphate Nitrate ..	454.00	400.00	435.00	438.00	442.30	443.00	435.00

* Except in the case of Madras, prices are exclusive of sales tax and other local taxes whereas in the case of Madras they are inclusive of sales tax. For sales in quantities not exceeding 5 kilograms at a time dealers may charge 1 paisa per kilogram in addition to the prices specified.

Note: The total cost including handling charges, transport subsidies, off-season rebate, railway freight, etc. incurred by the Fertilizers Pool in 1964-65 is estimated at Rs. 66.89 crores; incidental expenditures including establishment charges at Rs. 0.74 crore and the sales tax borne by the Pool at Rs. 0.31 crore. There is an estimated loss of Rs. 0.37 crore. The break-up of the Pool price is, therefore, as follows: Cost including transport etc. 98.98%; Estimated profit (—) 0.54%; Sales tax 0.46%; Incidentals 1.10%; Total 100.00%.

[Eastern Econ., 44 (1965), 2, 95]

STATISTICS

TABLE 1—AGRICULTURAL PRODUCTION IN INDIA: 1950-51 TO 1963-64

(000 metric ton)

Commodity	1950-51	1955-56	1960-61	1961-62	1962-63 (*Final estimates*)	1963-64 (*Provisional estimates*)
Foodgrains						
Cereals						
Rice	20,575	27,557	34,198	34,807	32,018	36,489
Wheat	6,462	8,760	10,992	12,039	11,132	9,708
Jowar	5,495	6,725	9,363	7,741	9,339	9,227
Bajra	2,595	3,428	3,228	3,554	3,862	3,786
Maize	1,729	2,602	4,015	4,269	4,520	4,527
Ragi	1,429	1,846	1,681	1,873	1,914	1,852
Barley	2,377	2,815	2,866	3,152	2,474	1,985
Small millets	1,750	2,070	1,975	1,970	1,841	2,031
TOTAL CEREALS	42,412	55,803	68,318	69,406	67,100	69,555
Pulses						
Gram	3,650	5,418	6,324	5,827	5,727	4,478
Tur	1,719	1,861	2,081	1,339	1,539	1,292
Other pulses	3,041	3,766	4,247	4,465	4,384	1,534**
TOTAL PULSES	8,410	11,045	12,652	11,631	11,650	7,304
TOTAL FOODGRAINS	50,822	66,848	80,970	81,037	78,750	76,859
Non-Foodgrains						
Groundnut	3,481	3,862	4,461	4,685	4,593	5,291
Castor seed	103	125	90	101	103	101
Cotton* (lint)	2,910	3,998	5,390	4,457	5,247	5,426
Jute	3,283	4,198	3,982	6,398	5,410	5,957
Mesta	—	1,153	1,131	1,706	1,534	1,819
Sugarcane (a)	5,705	6,075	10,615	10,144	9,371	10,288
Tea (b)	279	308	321	354	344	344
Coffee	19	35	68	46	56	70
Black pepper	21	28	28	28	26	24
Ginger (Dry)	14	16	17	17	17	20

* In thousand bales of 178 kgs each.

** Excluding other rabi pulses. In thousand bales of 181 kgs each.

(a) In terms of gur.

(b) Refers to calendar year.

Source: Ministry of Food and Agriculture.

[Records & Statistics, Quart. Bull. of Eastern Econ., 15 (1964), 4, 202]

TABLE 2—AGRICULTURAL PRODUCTION (TOTAL & PER CAPITA) IN SELECTED COUNTRIES

(Base: 1952-53 to 1956-57 = 100)

Country	*Agricultural Production (Total)*				*Agricultural Production (Per Capita)*			
	1955-56	1960-61	1961-62	1962-63	1955-56	1960-61	1961-62	1962-63
Europe								
United Kingdom ..	99	118	123	129	99	114	118	123
France	102	123	117	127	102	116	108	116
Germany, West ..	100	121	109	120	99	113	100	109
Italy	105	108	113	118	104	104	108	113
Belgium-Luxembourg ..	107	113	113	118	107	109	108	113
Sweden	90	90	103	101	89	96	99	96
Switzerland	99	110	110	110	98	100	98	95
Netherlands	104	118	120	121	102	109	109	109
Yogoslavia	120	143	129	136	118	135	120	125
North America								
Canada	99	108	91	116	96	92	76	96
United States ..	101	110	110	111	100	99	98	98
Latin America								
Argentina	97	102	110	108	96	92	97	94
Brazil	106	135	144	133	103	111	115	103
Mexico	111	146	149	158	108	122	121	124
Uruguay	97	91	93	99	96	83	84	87
Venezuela	105	127	133	145	101	103	104	110
Far East								
Burma	97	113	113	121	96	102	96	101
Ceylon	108	117	123	128	105	100	103	104
India	103	118	119	119	101	104	103	100
Indonesia	101	110	107	113	99	96	92	95
Japan	114	123	123	131	113	116	115	121
Pakistan	97	111	114	111	95	97	98	94
Thailand	105	131	140	146	102	110	114	116
Africa and Near East								
Iran	104	117	126	124	102	104	109	104
Iraq	89	102	108	120	86	86	89	97
South Africa ..	102	122	133	134	100	105	112	111
United Arab Republic ..	103	127	113	132	101	111	96	109
Oceania								
Australia	104	124	127	133	102	108	109	112
New Zealand ..	103	122	125	129	101	108	107	108

Source: F.A.O.

[Records & Statistics, Quart. Bull. of Eastern Econ. 15, (1964), 4, 203]

TABLE 3—CONSUMPTION OF FERTILIZERS PER UNIT AREA OF AGRICULTURAL LAND 1963-64

State	Consumption in lb. per acre				Consumption in kg. per hectare			
	N	P_2O_5	K_2O	Total	N	P_2O_5	K_2O	Total
Andhra Pradesh ..	4.87	1.95	0.10	6.92	5.46	2.19	0.11	7.76
Assam	0.14	0.16	0.12	0.42	0.16	0.18	0.13	0.47
Bihar	1.31	0.55	0.25	2.11	1.47	0.62	0.28	2.37
Gujarat & Maharashtra* ..	1.82	0.79	0.23	2.84	2.04	0.89	0.26	3.19
Jammu & Kashmir ..	1.14	0.02	—	1.16	1.28	0.02	—	1.30
Kerala	4.20	1.18	3.56	8.94	4.71	1.32	3.99	10.02
Madhya Pradesh ..	0.34	0.18	—	0.52	0.38	0.20	—	0.58
Madras	5.56	1.29	1.37	8.22	6.23	1.45	1.54	9.22
Mysore	1.78	0.71	0.51	3.00	2.00	0.80	0.57	3.37
Orissa	0.40	0.10	0.06	0.56	0.45	0.11	0.07	0.63
Punjab	4.01	0.25	0.01	4.27	4.50	0.28	0.01	4.79
Rajasthan	0.34	0.10	—	0.44	0.38	0.11	—	0.49
Uttar Pradesh	2.75	0.24	0.01	3.00	3.08	0.27	0.01	3.36
West Bengal	2.38	1.06	0.80	4.24	2.67	1.19	0.90	4.76
Delhi	1.17	0.33	—	1.50	1.31	0.37	—	1.68
Himachal Pradesh ..	0.71	0.48	—	1.19	0.80	0.54	—	1.34
Manipur	0.99	0.22	—	1.21	1.11	0.25	—	1.36
Tripura	0.05	—	—	0.05	0.06	—	—	0.06
TOTAL ..	2.24	0.64	0.27	3.15	2.51	0.72	0.30	3.53

* Separate figures of agricultural area in the two states are not available.

Note: 1. Calculated on the basis of distribution figures.

[FAI Inf. Serv., 5 (1964), 22, 9-10]

TABLE 4—LAND UTILISATION

(*In Million acres*)

	1950-51	1961-6
Total geographical area*	806.3	806.3
Total reporting area	702.5	738.4
Forests	100.0	137.8
Not available for cultivation		
(*i*) Land put to non-agricultural uses	27.7	35.6
(*ii*) Barren and uncultivable land	89.7	85.2
TOTAL ..	117.4	120.8
Other Uncultivated land (exclu. fallow lands)		
(*i*) Permanent pastures & grazing lands	16.5	34.4
(*ii*) Land under tree crops & groves	49.0	14.0
(*iii*) Cultivable waste	56.7	44.8
TOTAL ..	122.2	93.2
Fallow lands		
(*i*) Current fallows	26.4	26.5
(*ii*) Others	43.1	26.1
TOTAL ..	69.5	52.6
Net area sown	293.4	334.0
Area sown more than once	32.5	50.6
Total cropped area	325.9	384.6
Net area irrigated	51.5	61.2
Area irrigated more than once	4.3	8.9
Gross area irrigated	55.8	70.1

* Excluding Pondicherry

[Eastern Econ., Annual No. (1965), 1349]

TABLE 5—CONSUMPTION OF FERTILIZERS

(*Thousand tonnes*)

Year	*Nitrogen (N)*	*Phosphate (P_2O_5)*	*Potash (K_2O)*	*Total*
1947	4.3	0.9	1.8	7.0
1951	58.7	6.9	7.7	73.3
1955	111.0	12.8	10.2	134.0
1960	231.8	53.8	29.6	315.2
1961	307.1	63.6	30.4	401.1
1962	327.8	91.2	39.9	458.9
1963	439.9	130.6	56.5	627.0
1965 (anticipated)	650.0	250.0	150.0	1050.0
1965 (Target)	1000.0	400.0	200.0	1600.0
1970 (Tentative target)	2000.0	1000.0	350.0	3350.0

[Eastern Econ., Annual No. (1965), 1349]

TABLE 6—RANKING OF STATES BY GROSS AND NET VALUE OF AGRICULTURAL OUTPUT: 1960-61

	Gross Value of Output per acre		*Net Value of Output per acre*		*Net Output per Worker*	
	Rupees	*Index* (*All States:* 100)	*Rupees*	*Index* (*All States:* 100)	*Rupees*	*Index* (*All States:* 100)
Kerala	521.56	278.6	445.44	277.3	1,159	243.0
Assam	370.87	198.1	347.78	216.5	620	130.0
West Bengal	348.84	186.3	313.21	195.0	824	172.7
Madras	338.92	181.0	282.87	176.1	530	111.1
Jammu & Kashmir	261.82	139.9	231.11	143.9	395	76.5
Orissa	208.21	111.2	180.80	112.5	488	102.3
Uttar Pradesh	199.88	106.8	167.09	104.0	479	100.4
Andhra Pradesh	188.23	100.5	156.65	97.5	365	75.5
Delhi	187.05	99.9	164.73	102.5	800	167.7
Bihar	186.83	99.8	161.53	100.5	302	63.3
Punjab	175.83	93.9	155.55	96.8	861	180.5
Mysore	167.41	89.4	137.94	86.3	476	99.8
Himachal Pradesh	164.13	87.7	136.04	84.7	214	44.9
Gujarat	153.10	81.8	136.77	85.1	578	121.2
Maharashtra	152.24	81.3	132.08	82.2	467	97.9
Madhya Pradesh	125.29	66.9	106.10	66.0	360	82.8
Rajasthan	84.41	45.1	71.34	44.4	343	71.9
All States	187.21	100.0	160.61	100.0	477	100.0

Source: National Council of Applied Economic Research.

[Eastern Econ., Annual No. (1965), 1349]

TABLE 7—Yield Per Hectare of Principal Crops

(Quintals per Hectare)

Crop	1950-51	1955-56	1960-61	1962-63	1963-64
Foodgrains					
Rice	6.7	7.8	10.2	9.1	10.3
Wheat	6.6	7.1	8.5	7.9	7.3
Jowar	3.5	3.9	5.4	5.3	5.1
Bajra	2.9	3.0	2.8	3.6	3.5
Maize	5.5	7.0	9.2	9.9	10.0
Barley	7.6	8.2	8.8	8.0	7.1
Small Millet	3.8	3.9	4.0	4.0	4.4
Gram	4.8	5.5	6.7	5.8	4.9
Oilseeds					
Groundnuts	7.7	7.5	7.1	7.0	7.8
Sesamum	2.0	2.0	1.5	1.9	1.8
Rape & Mustard	3.7	3.4	4.7	4.2	3.0
Linseed	2.6	2.7	2.2	2.3	2.0
Fibres					
Cotton (Lint)	0.9	0.9	1.3	1.2	1.2
Jute	10.4	10.8	11.8	11.6	12.5
Miscellaneous					
Sugarcane (gur)	33.4	32.9	45.3	41.9	46.5
Tobacco	7.3	7.4	7.8	8.8	8.5

Note: 1 quintal = 100 Kgs. Hectare = 10,000 square metres

[Easter Econ., Annual No. (1965), 1351]

TABLE 8—INDEX NUMBERS OF AGRICULTURAL PRODUCTION: 1950-51 TO 1963-64

(Agricultural Year 1949-50 = 100)

Commodity/Group	Weight	1950-51	1955-56	1960-61	1961-62	1962-63	1963-64
1. Foodgrains							
Rice	35.3	87.9	114.2	136.2	139.0	127.4	145.7
Jowar	5.0	89.8	96.7	134.6	111.2	138.4	132.5
Bajra	2.7	83.8	108.3	101.2	111.3	121.9	117.0
Maize	2.1	84.4	112.3	144.4	152.3	163.5	161.7
Wheat	8.5	101.1	131.3	162.7	178.3	160.4	143.8
Barley	2.0	105.6	118.5	120.0	133.6	102.7	84.1
Cereals	58.3	90.3	114.9	136.6	140.0	132.4	139.9
Grams	3.7	98.0	138.9	162.3	149.5	137.1	114.9
Tur	1.1	91.8	99.4	106.8	68.7	80.5	65.3
Pulses	8.6	91.7	118.4	128.6	120.3	116.9	101.2
Foodgrains	66.9	90.5	115.3	135.6	137.5	130.4	134.9
2. Non-Foodgrains							
Groundnut ..	5.7	101.4	112.4	131.7	138.3	142.3	156.2
Sesamum ..	1.2	101.6	104.8	78.0	92.1	112.1	99.1
Rapeseed & Mustard	2.0	94.6	105.8	166.9	164.5	159.3	111.9
Oilseeds	9.9	98.5	108.6	128.0	134.4	137.7	133.6
Cotton	2.8	110.7	153.9	203.3	170.2	201.8	206.3
Jute	1.4	106.3	135.8	121.6	193.8	165.1	180.5
Fibres	4.5	108.6	149.7	175.7	183.2	193.6	202.4
Tea	3.3	103.8	107.2	120.9	133.5	129.1	129.2
Coffee	0.2	112.3	196.1	355.1	240.1	278.8	278.8
Rubber	0.1	93.8	146.1	165.3	176.3	204.8	243.0
Plantation Crops ..	3.6	104.0	113.2	135.1	140.6	139.5	140.7
Sugarcane ..	8.7	113.7	119.8	173.9	163.7	154.0	165.5
Tobacco	1.9	97.3	112.9	116.3	129.6	136.0	125.0
Pepper (Black) ..	1.2	97.2	132.6	134.4	134.6	123.8	112.8
Miscellaneous Crops ..	15.1	110.3	120.1	155.8	150.8	149.7	151.4
Non-Foodgrains ..	33.1	105.9	119.9	147.9	149.2	151.0	151.8
All-Commodities ..	100.0	95.6	116.8	139.7	141.4	137.2	140.5

[Eastern Econ., Annual No. (1965), 1352]

TABLE 9—DISTRIBUTION OF AGRICULTURAL OUTLAYS IN PUBLIC SECTOR

(Rs. Crores)

	First Plan (1951-52 to 1955-56)	*Second Plan* (1956-57 to 1960-61)	*Third Plan* (1961-62 to 1965-66)	*Fourth Plan* (1966-67 to 1970-71)
I. **Agriculture**	289.8	529.0	1,098.7	2,400.0
Agricultural production (including minor irrigation) ..	176.1	192.0	402.8	1,224.0
Animal husbandry (including dairying and milk supply) ..	15.5	33.5	90.5	210.0
Fisheries	2.7	9.1	26.4	110.0
Forests and soil conservation	11.5	36.9	124.1	335.0
Co-operation (including marketing and storage) ..	5.0	38.8	132.9	261.0
Community Development	79.0	218.7	322.0	260.0
II. **Irrigation**	310.0	420.0	648.0	1,000.0
TOTAL OUTLAY	599.8	949.0	1,746.7	3,400.0

[Eastern Econ., Annual No. (1965), 1355]

TABLE 10—TENTATIVE TARGETS OF DEVELOPMENT

Programmes	*Unit*	*Third Plan*		*Fourth Plan Proposed Target*
		Target	*Anticipated*	
1. Irrigation				
(*a*) Major	(Million acres)	12.80	7.70	14.00
(*b*) Minor	(Million acres)	12.80	13.80	17.00
2. Soil Conservation	(Million acres)	11.00	11.80	20.00
3. Land Reclamation	(Million acres)	3.60	3.00	2.50
4. Extension of area through double cropping	(Million acres)	—	—	22.50
5. Consumption of chemical fertilisers				
(*a*) Nitrogenous (N)	(Million tonnes)	1.00	0.65	2.00
(*b*) Phosphatic (P_2O_5)	(Million tonnes)	0.40	0.25	1.00
(*c*) Potassic (K_2O)	(Million tonnes)	0.20	0.15	0.35
6. Area under improved seeds—foodgrains	(Million acres)	204.00	164.00	274.00
7. Organic and green manures				
(*a*) Urban compost	(Million tonnes)	5.00	4.42	5.40
(*b*) Green manures	(Million acres)	41.00	27.90	64.00
8. Plant protection	(Million acres)	50.00	40.00	160.00

[Eastern Econ., Annual No. (1965), 1355]

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